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#### COMMUNICATION

Bulk binary ZrO<sub>2</sub>-based oxides as highly active alternative-type

Received 00th January 20xx, Accepted 00th January 20xx DOI: 10.1039/x0xx00000x

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catalysts for non-oxidative isobutane dehydrogenation

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Bulk binary  $ZrO_2$ -based oxides efficiently catalyse non-oxidative isobutane dehydrogenation to isobutylene. Their activity strongly depends on the kind of second metal oxide. So designed  $CrZrO_x$ showed superior activity to industrially relevant catalysts with supported Pt or  $CrO_x$  species. It was also stable under alternating dehydrogenation and oxidative regeneration cycles over ca. 110 h under different reaction conditions between 550 and 600°C.

Isobutylene is an important building block in the chemical industry used for the manufacture of polymers, solvents, dyes, resins, fibres, and drugs. It is mainly produced as by-product in steam cracking of naphtha and fluid catalytic cracking of heavier oil fractions. Isobutylene can also be directly generated from isobutane through dehydrogenation (DH) of the latter in the presence or in the absence of oxidising agent. The former approach is still not used on an industrial scale because of too low selectivity to the desired olefin at industrially relevant degrees of alkane conversion. Compared with the oxidative dehydrogenation, the non-oxidative dehydrogenation of isobutane has been commercialized<sup>1, 2</sup> and the share of isobutylene production through such technology expected to grow. Consequently, demand is for dehydrogenation catalysts will also increase.

Supported catalysts with DH active  $CrO_x$  or Pt-Sn species are commercially applied for the target reaction.<sup>1-4</sup> Their activity drops with time on stream due to blockage of active sites by coke. As a consequence, the catalysts must be oxidatively regenerated. However, catalytically active  $CrO_x$  or Pt-Sn species undergo restructuring in a sequence of dehydrogenation/regeneration cycles that shortens catalyst lifetime. Moreover, Pt is expensive and limitedly available, while some chromium compounds are toxic.

With the purpose to overcome the above drawbacks, various research groups in the world have attempted to improve

available commercial catalysts or to develop suitable alternatives. The literature on unconventional catalyst compositions is scarce.<sup>1</sup> Supported VO<sub>x</sub>-containing catalysts were concluded to be the most promising materials. For example, Mondal et al.<sup>5</sup> reported an isobutylene yield of ca. 35% at an isobutane conversion of 40% using a  $ZrV_2O_7$  catalyst at 550°C. The selectivity to isobutylene of around 85% was achieved over VO<sub>x</sub>/Al<sub>2</sub>O<sub>3</sub> at isobutane conversion of 50%.<sup>6</sup> To increase isobutylene production and on-stream stability, Ovsitser et al.<sup>7</sup> performed isobutane dehydrogenation over VO<sub>x</sub>/MCM-41 under oxygen-lean conditions. In comparison with pure oxidative isobutane dehydrogenation, the selectivity to isobutylene was improved from 60% to 80% with a simultaneous increase in the conversion of isobutane from 5% to 50% respectively. A similar performance was achieved when isobutane was dehydrogenated in the presence of CO2 over activated carbon with supported FeO<sub>x</sub> species.<sup>8</sup> Isobutane DH was also investigated over supported catalysts with sulphides of Zn, Cu, Mn, Mo, Fe, Co and Ni.9-11 Among these catalysts, CoS/SiO<sub>2</sub> showed both the highest selectivity to isobutylene (87 %) and the highest isobutane conversion of 71% at 600°C. This performance was, however, achieved with a diluted reaction feed (14 vol.% isobutane in nitrogen).

We have recently introduced suitable alternatives for propane DH catalysts that consist of  $ZrO_2$  doped with  $La_2O_3$  and possess tiny amounts (up to 0.05 weight %) of Ru, Rh or Cu on their surface.<sup>12</sup> Coordinatively unsaturated Zr cations ( $Zr_{cus}$ ) were identified to be active DH sites, while the supported metals contributed to generation of such sites through  $ZrO_2$  reduction.

Using this fundamental knowledge, we developed a new family of binary  $ZrO_2$ -based catalysts for isobutane DH to isobutylene. In contrast to our previous propane DH study,<sup>12</sup> these catalysts are free of any dehydrogenation-active supported metals. The kind of metal oxide promoter for  $ZrO_2$  was established to influence catalyst activity and selectivity. Such novel materials showed close or even superior activity to industrially relevant Pt(0.5 wt.%)-Sn(1.7 wt.%)/Al\_2O\_3 (Pt-Sn/Al\_2O\_3) and CrO\_x(19.6 wt.%)-K(0.9 wt.%)/Al\_2O\_3 (Cr-K/Al\_2O\_3) under the same reaction

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Electronic Supplementary Information (ESI) available: Materials preparation, details of catalysts characterisation and testing. See DOI: 10.1039/x0xx00000x

#### COMMUNICATION

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DOI: 10.1039/C6CC02813F Journal Name

conditions. Their practical relevance was proven in a series of 30 dehydrogenation/regeneration cycles at 550°C and 600°C lasting in total over 110 hours.

Table 1 Selected physico-chemical properties, isobutane conversion (X), space time yield (STY) of isobutylene and isobutylene selectivity (S). Test conditions: 550°C, iso- $C_4H_{10}$ : $N_2$ =40:60, contact time of 0.24 g·s·ml<sup>-1</sup>.

Dopant	SBET	Х	S	STY
/ mol.%	/ m <sup>2</sup> ⋅g <sup>-1</sup>	/-	/-	/ kg·h <sup>-1</sup> ·m <sup>-3</sup>
0	38	0.04	0.94	695
8	120	0.07	0.83	803
9	72	0.15	0.91	1883
10	135	0.36	0.84	5861
10	75	0.02	0.88	310
10	51	0.01	0.78	177
10	60	0.13	0.80	2037
	Dopant / mol.% 0 8 9 10 10 10 10 10	Dopant SBET   / mol.% / m <sup>2</sup> ·g <sup>-1</sup> 0 38   8 120   9 72   10 135   10 75   10 51   10 60	$\begin{array}{c c c c c c c c c c c c c c c c c c c $	Dopant S <sub>BET</sub> X S   / mol.% / m <sup>2</sup> ·g <sup>-1</sup> / - / -   0 38 0.04 0.94   8 120 0.07 0.83   9 72 0.15 0.91   10 135 0.36 0.84   10 75 0.02 0.88   10 51 0.01 0.78   10 60 0.13 0.80

Pure  $ZrO_2$  and binary oxides with exception of  $La_8Zr_{92}O_x$  and  $Y_9Zr_{91}O_x$  were prepared from of  $ZrOCl_2 \cdot 8H_2O$  and nitrates (or chloride in case of Ga) of corresponding second metal using an aqueous solution of ammonia as a precipitating agent. The formed precipitate was washed several times with deionized water until chloride ions were not identified in the filtrate (reaction with AgNO<sub>3</sub>). All solids were finally calcined at 550°C for 4h.  $La_8Zr_{92}O_x$  and  $Y_9Zr_{91}O_x$  are commercial materials from MEL Chemicals. According to X-ray diffraction analysis, bare ZrO<sub>2</sub> was composed of monoclinic main phase and a small amount of tetragonal modification while all binary materials with a ratio of  $Zr/dopant \leq 11.5$  were stabilized in the tetragonal phase after calcination at 550°C (Figure S1 in the Electronic Supporting Information (ESI)). A similar stabilization effect of oxide dopants in ZrO2-based materials has been documented in several previous studies.<sup>13, 14</sup> It is related to formation of oxygen vacancies for charge compensation or due to distortion of ZrO<sub>2</sub> lattice.

The developed materials were initially tested for their activity and selectivity in the non-oxidative dehydrogenation of isobutane to isobutylene at 550°C using a feed with 40 vol.% isobutane in nitrogen. The latter feed component was used as an internal standard to take into account reaction-induced changes in number of moles when calculating the isobutane conversion, selectivity and space time yield (STY) of isobutylene formation (Equations S1-S3 in ESI). Isobutylene, 1and 2- butenes, methane as well as  $C_{2}$ - and  $C_{3}$ -hydrocarbons were the detected carbon-containing gas-phase products. For all catalysts, the conversion of isobutane decreased within 45 min DH cycle (Figure S2 in ESI). Selected initial (after 9 min on stream) catalytic data are summarized in Table 1. It is obvious that the catalysts strongly differ in their activity for isobutane dehydrogenation. Doping  $ZrO_2$  with  $In_2O_3$  or  $Al_2O_3$  has a negative effect on the activity, while other doped catalysts performed superior to bare ZrO<sub>2</sub>; the highest conversion of around 0.36 was obtained over  $Cr_{10}Zr_{90}O_x$ . Such positive effect of the dopants cannot be simply explained by the difference in specific surface area (Table 1) thus highlighting the importance of the kind of metal oxide dopant for isobutane dehydrogenation. Doping also influences the selectivity to

isobutylene and STY of this olefin. Oxides of yttrium, gallium and chromium are the most attractive dopants in terms of isobutylene productivity.

To check if the high activity of  $Cr_{10}Zr_{90}O_x$  is related to the presence of well-known DH active CrO<sub>x</sub>, we prepared three additional catalysts. Two of them were binary oxides synthesized according to the same protocol as for Cr<sub>10</sub>Zr<sub>90</sub>O<sub>x</sub> but contained 2 and 5 times lower amount of chromium. They are abbreviated as  $Cr_5Zr_{95}O_x$  and  $Cr_2Zr_{98}O_x$  and were composed of monoclinic and tetragonal phases with the former fraction increasing with a decrease in Cr loading (Figure S1 in ESI). The third material was a supported catalyst with 0.5 wt.% Cr<sub>2</sub>O<sub>3</sub> on La<sub>8</sub>Zr<sub>92</sub>O<sub>x</sub> possessing stabilized tetragonal ZrO<sub>2</sub> phase; an apparent Cr surface density was around 0.3 Cr nm<sup>-2</sup> as calculated from the nominal concentration of Cr and the sample specific surface area. Since the binary CrZrO<sub>x</sub> materials contain Cr not only on their surface but also in the bulk, this calculation method is not applicable for these catalysts. Therefore, we used the below procedure to estimated surface concentration of Cr in the binary materials.

We initially used XPS to determine atomic ratio of Zr/Cr in the near-surface region. It was 11 and 17 for  $Cr_{10}Zr_{90}O_x$  and  $Cr_5Zr_{95}O_x$  and close to the nominal values of 9 and 19 respectively. The concentration of Cr on the surface of Cr<sub>2</sub>Zr<sub>98</sub>O<sub>x</sub> was too low to be determined precisely. Nevertheless, the XPS results exclude any enrichment of Cr at the surface and indicate that Cr is incorporated in the ZrO<sub>2</sub> structure forming a solid solution. On the basis of previous characterisation study of Morterra et al.<sup>15</sup>, the (101) face is the most preferentially exposed plane in polycrystalline tetragonal ZrO<sub>2</sub>. Under this assumption, around 8.6 surface atoms of Zr are located in one square nanometre. Using this value and the nominal concentration of Cr, we calculated an apparent surface density of this metal in the binary  $CrZrO_x$  oxide materials. Despite the fact that  $Cr_5Zr_{95}O_x$  and  $Cr_2Zr_{98}O_x$  are composed of monoclinic and tetragonal modifications, our estimation should also be valid for these materials because the number of surface Zr atoms in one square nanometre of tetragonal ZrO<sub>2</sub> is close to 8.1 and 9.0 on the most stable (111) and (111) surfaces of monoclinic zirconia respectively.<sup>16, 17</sup>

Figure 1 illustrates the effect of Cr surface density on the apparent turnover frequency (TOF) of isobutane conversion, i.e. the activity related to one surface Cr atom (Equations S4-S6 in ESI). Essentially, the TOF values over the CrZrO<sub>x</sub> catalysts decreased with Cr loading. Such behaviour can only be explained when assuming that Cr-containing sites should not be the only active ones in these catalysts. From a mechanistic viewpoint, there are no doubts that CrOx species on the surface of CrO<sub>x</sub>/La<sub>8</sub>Zr<sub>92</sub>O<sub>x</sub> catalyse isobutane dehydrogenation.<sup>1</sup> This statement is actually supported by the fact that this catalyst is significantly more active than La<sub>8</sub>Zr<sub>92</sub>O<sub>x</sub> (Table 1 and Figure 1).

It is also important to mention that the binary  $CrZrO_x$  catalysts showed higher STY values than the supported reference material despite the fact that one of them had lower surface density of Cr (Figure 1). This result clearly demonstrates the advantage of bulk doping of  $ZrO_2$  over surface modification or



Figure 1 Effect of apparent surface density of chromium on turn over frequency of isobutane (TOF) conversion (black squares) and space time yield (STY) of isobutylene formation (grey bars) over binary  $CrZrO_x$  catalysts (filled symbols) and a supported  $CrO_x/La_z Zr_{92}O_x$  catalyst (open symbols) at 550°C.

grafting with  $CrO_x$  species for achieving high isobutylene DH activity. A possible explanation for this effect is given below.

To test whether bulk structure of binary oxides is changed after high-temperature treatment under reducing conditions, we applied XRD analysis for monitoring possible phase changes in  $Cr_{10}Zr_{90}O_x$  upon its heating to 750°C in a H<sub>2</sub>-containing flow. The only detected phase was tetragonal zirconia (Figure S1 in ESI). In addition, XPS analysis proved that surface Cr concentration in the reduced catalyst did not increase after such treatment. Thus, any enrichment of Cr at the surface upon reductive catalyst treatment can be excluded. However, the XP spectra of  $Zr3d_{5/2}$  in oxidized and reduced  $Cr_{10}Zr_{90}O_x$ differ significantly (Figure S3 in ESI). As expected, Zr<sup>4+</sup> is the only state in the former ( $E_{B}$  = 182.2 eV for Zr3d<sub>5/2</sub>).<sup>18</sup> The Zr 3d spectrum in the reduced sample cannot be well-resolved as in the oxidized counterpart. Unambiguously, a feature at lower binding energies appeared thus indicating the formation of Zr suboxides with an O/Zr ratio lower than 2.<sup>19</sup> In other words, anion vacancies should be formed in the lattice of ZrO<sub>2</sub>. Taking the above results into account, we put forward that, in addition to Cr sites,  $Zr_{cus}$  (located at anion vacancies) also participate in isobutane dehydrogenation over bulk binary ZrO<sub>2</sub>-based oxides as previously concluded for propane DH.<sup>12</sup> Such sites are formed upon removal of surface lattice oxygen in situ under reaction conditions.

To benchmark our materials, we determined their dehydrogenation performance in the same set-up together with two industrially relevant reference materials, i.e. Cr-K/Al<sub>2</sub>O<sub>3</sub> and Pt-Sn/Al<sub>2</sub>O<sub>3</sub> prepared according to Ref.<sup>20</sup> and Ref.<sup>21</sup> respectively. The tests were performed at 550°C with both oxidized and prereduced materials. For a proper comparison of the catalysts, we use STY of isobutylene formation at the initial isobutane conversion of around 0.4. To fulfil this requirement, catalytic tests were carried out at different contact times by varying both catalyst amount and total flow. Figure 2 shows the initial STY values obtained over bare ZrO<sub>2</sub>, ZrO<sub>2</sub> doped with La<sub>2</sub>O<sub>3</sub>, Y<sub>2</sub>O<sub>3</sub> or Cr<sub>2</sub>O<sub>3</sub> as well as over Cr-K/Al<sub>2</sub>O<sub>3</sub> and Pt-Sn/Al<sub>2</sub>O<sub>3</sub>.



DOI: 10.1039/C6CC02813

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Figure 2 Space time yield of isobutylene formation at isobutane conversion of around 0.4 over oxidized (black bars) or reduced (grey bars) catalysts at 550°C with iso- $C_{\rm g}H_{10}$ :N<sub>2</sub>=40:60.

There is no difference in the activity between reduced and oxidized  $Cr-K/Al_2O_3$ , while a positive effect of reductive treatment was observed for all other catalysts. Reduced Pt-Sn/Al\_2O\_3 showed significantly higher activity than the oxidized material owing to the formation of metallic Pt upon catalyst reduction before starting isobutane dehydrogenation. It is well established that such species catalyse this reaction.<sup>1</sup>

All reduced binary  $ZrO_2$ -based catalysts were slightly active than their oxidized counterparts. This is due to the fact that DH active  $Zr_{cus}^{4+}$  species were generated during reductive treatment of the catalysts.<sup>12</sup> The effect of catalyst treatment was, however, less pronounced than for Pt-Sn/Al<sub>2</sub>O<sub>3</sub>.

Another important result shown in Figure 2 is the high activity of our binary catalysts. The STY value obtained over Cr<sub>10</sub>Zr<sub>90</sub>O<sub>x</sub> was about two times higher than for Cr-K/Al<sub>2</sub>O<sub>3</sub> and even slightly (around 15%) higher than for reduced Pt-Sn/Al<sub>2</sub>O<sub>3</sub>. The practical relevance of  $Cr_{10}Zr_{90}O_x$  was demonstrated over ca. 110 hours on stream in a series of 30 DH/oxidative regeneration cycles at 550 and 600°C. Each DH cycles lasted over 27 min, while the regeneration continued for 15 min at the same DH temperature. No reductive pre-treatment was performed. Commercially like Cr-K/Al<sub>2</sub>O<sub>3</sub> and Pt-Sn/Al<sub>2</sub>O<sub>3</sub> catalysts were also tested under the same reaction conditions. The maximal STY of isobutylene formed over the catalysts in each dehydrogenation cycle is given in Figure 3. The corresponding isobutane conversion values and an overall amount of isobutylene generated in each cycle are shown in Figure S4 in ESI. Low long-term stability of oxidized Pt-Sn/Al<sub>2</sub>O<sub>3</sub> is in agreement with our previous study on propane DH<sup>22</sup> and should be related to restructuring Pt species upon oxidative catalyst regeneration.<sup>21</sup>

In terms of STY, the  $Cr_{10}Zr_{90}O_x$  catalyst performed superior to  $Cr-K/Al_2O_3$  and  $Pt-Sn/Al_2O_3$  at 550°C. The lower performance of  $Cr_{10}Zr_{90}O_x$  at 600°C is due to very fast catalyst deactivation. Nevertheless,  $Cr_{10}Zr_{90}O_x$  restored its high isobutylene productivity when the DH reaction was again performed at 550°C. The catalyst did not change its performance from cycle to cycle and did not undergo any severe structural changes as proven by XRD analysis (Figure S5 in ESI). Moreover, it also showed isobutylene selectivity above 85%. The main side



Figure 3 Maximal STY of isobutylene formed over Cr<sub>10</sub>Zr<sub>90</sub>O<sub>x</sub> (•), Cr-K/Al<sub>2</sub>O<sub>3</sub> (•) and Pt-Sn/Al<sub>2</sub>O<sub>3</sub> (▲) in a series of 30 DH/regeneration cycles at 550°C and 600°C with WHSV of 7.75 and 15.5 h<sup>-1</sup> respectively. In total, the catalysts were under high-temperature treatment (dehydrogenation, regeneration and purging with N2) over 110 h. Further experimental details are reported in ESI.

products were light hydrocarbons and coke. The latter could be completely removed during regeneration within only 5 min on air stream at the PDH temperature.

In summary, we successfully demonstrated that bulk promoting of ZrO<sub>2</sub> with different metal oxides results in active and selective catalysts for non-oxidative dehydrogenation of isobutane to isobutylene. In comparison with typically applied supported materials, surface defects in the lattice of ZrO<sub>2</sub> were identified to be the active sites. They are  $Zr_{cus}$  and cations of DH active metal in the lattice of binary ZrO<sub>2</sub>-based oxide materials. This valuable information establishes the essential basis to design alternative highly active catalysts for nonoxidative dehydrogenation of isobutane.

T.O. acknowledges support from DAAD (German Academic Exchange Service) and the Ministry of Education and Science of the Russian Federation.

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DOI: 10.1039/C6CC02813F

Journal Name