

Studies on the effects of CO₂ and CO on *n*-butane isomerisation activity over sulfated zirconia

H.K. Mishra^a, A.K. Dalai^{a,*}, K.M. Parida^b

^a Catalysis and Chemical Reaction Engineering Laboratories, Department of Chemical Engineering, 110 Science Place, University of Saskatchewan, Saskatoon, Canada S7N 5C9

^b Environment Management and Inorganic Chemicals Division, Regional Research Laboratory (CSIR), Bhubaneswar 751 013, Orissa, India

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Abstract

Sulfated zirconia with 10 wt.% nominal sulfate loading was synthesised, characterised and tested for *n*-butane isomerisation activity varying butane diluents such as CO₂, CO and nitrogen, and reaction temperatures. Results revealed that a fresh, air-pre-treated catalyst was poisoned by CO₂, and exhibited low catalytic activity, whereas an air-regenerated catalyst showed high butane conversion with negligible catalyst deactivation in presence of CO₂. Incorporation of CO in the feed stream poisoned the catalyst immediately and removal of CO from the feed regenerated the catalyst activity. The reversible poisoning effect of CO was prominent at low temperature and was absent at elevated temperatures. It seems that the surface oxy species of sulfated zirconia, both the lattice and the adsorbed, play an important role in butane isomerisation and catalyst poisoning by CO₂, whereas, formation of surface stabilised adspecies causes the negative effect of CO. © 2002 Elsevier Science B.V. All rights reserved.

Keywords: Sulfated zirconia; Isomerisation; Diluent effects; Oxy species

1. Introduction

Research in sulfated zirconia has drawn much attention after Arata first reported butane isomerisation over this catalyst at room temperature [1]. Since then the properties of sulfated zirconia and its possible applications, especially in *n*-butane isomerisation, have been explored and described extensively in literature.

The current research in sulfated zirconia is still concentrated on the basic aspects, e.g. the nature of active sites [2,3], the reaction mechanism [4,5] and its rapid deactivation following contact with hydrocarbons [6].

Ability to isomerise butane was initially thought due to high acidity of the catalyst, and presence of Bronsted acid sites that directly protonate *n*-butane. However, the experimental facts later proved that sulfated zirconia is not super-acidic, and direct protonation of butane was thus abandoned [7]. Attention also focused on the redox properties, and recently Mishra et al. [8], in agreement with earlier reports, showed that butane isomerisation proceeds via a redox scheme. For sulfated zirconia, sulfate groups were considered as the oxidising and active species in butane transformation mechanism; however, a recent report by Hong et al. [9] showed that zirconium oxy sites are the centers for butane activation. Another report by Wan et al. [10] showed that CO could irreversibly poison the iron–manganese promoted catalyst as CO is oxidised

* Corresponding author. Tel.: +1-306-966-4771;

fax: +1-306-966-4777.

E-mail address: dalai@enr.usask.ca (A.K. Dalai).

to CO₂ by the oxy species of the iron-oxy moiety formed by the interaction of air with the catalyst during calcination and/or pretreatment. Morterra et al. [11] conducted similar experiments as that of Wan et al. and found CO poisoning of the catalyst is reversible. Based on their observations, Morterra et al. proposed the low temperature activity of the catalyst is associated with Lewis acidity. More recently, Sayari et al. [12] performed CO and H₂ poisoning studies on iron manganese promoted sulfated zirconia in the temperature range 35–100 °C and found CO poisoning effect could be reversible or irreversible depending upon the reaction conditions. They concluded that the irreversible effect of CO is associated with destruction of the active sites, whereas the reversible effect is due to competitive adsorption of CO and butane on catalyst surface. Despite all these reports, no paper has dealt with either the effect of CO on butane isomerisation at elevated temperatures (>200 °C), or the effect of CO₂ on the activity of sulfated zirconia catalyst under different reaction conditions.

In this work, a detailed investigation on butane isomerisation was carried out varying reaction conditions, and butane diluents such as CO and CO₂. Results suggest that a process involving interaction between butane molecule and zirconium oxy species prevails in the initiation step of butane isomerisation, and these oxy species play a dominant role in catalyst poisoning by CO₂. The reversible poisoning effect of CO is probably related to the formation of adspecies, which are in dynamic equilibrium with the catalyst surface.

2. Experimental

2.1. Catalyst preparation

Details of the catalyst preparation are reported elsewhere [8]. In brief, the zirconium hydroxide was sulfated using ammonium peroxydisulfate. The sulfated zirconium hydroxide was calcined at 600 °C for 3 h in static air and kept in a glass vial for use. The zirconium hydroxide, used for the preparation of sulfated zirconia, was synthesised employing an organo-inorganic route, where acetyl acetone was used to slow down the rate of hydrolysis of ZrO²⁺, and sodium dodecyl sulfate was used to shape the precipitation medium.

Table 1

Physico-chemical properties of sulfated zirconia calcined at 600 °C

XRD phase ^a	Tetragonal + less monoclinic
BET surface area (m ² /g)	162
Pore radius (Å)	48.0
Pore volume (ml/g)	0.39
Lewis zirconia ^b	9.0
Bronsted zirconia ^b	10.9
Sulfur content (wt.%)	1.45

^a Ratio of tetragonal to monoclinic phase intensity is approximately 7.

^b Measured from photoacoustic study of adsorbed pyridine.

2.2. Catalyst characterisations

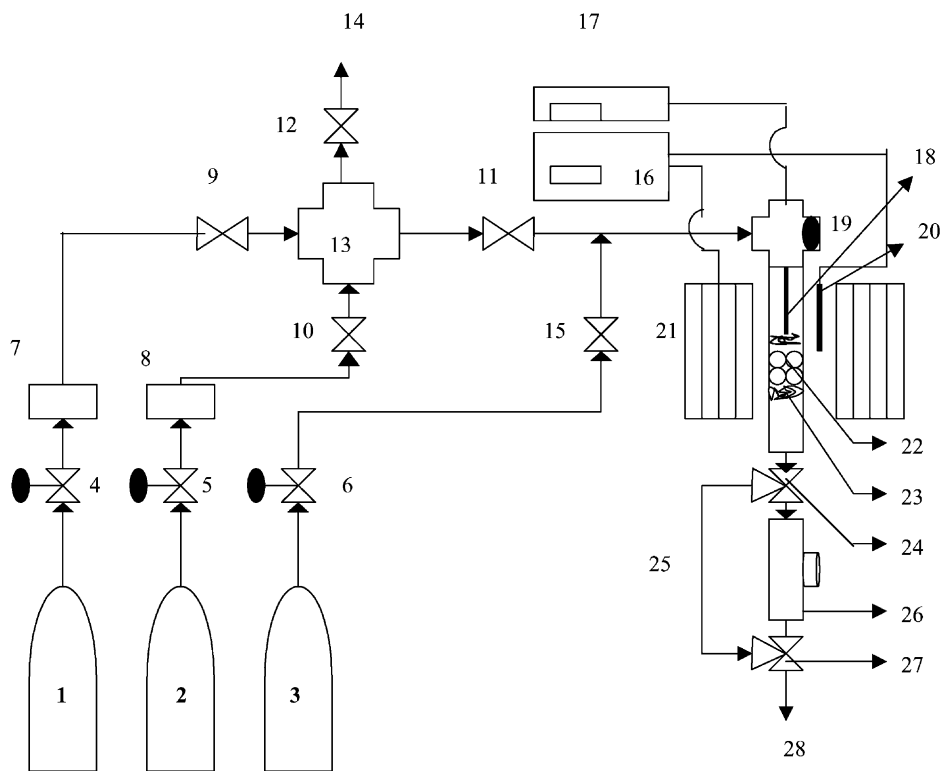
The details of the catalyst characterisations are reported elsewhere [8]. In brief, the surface area, pore volume and average pore diameter were determined from nitrogen adsorption–desorption isotherm, measured in a BET analyser (ASAP 2000 from Micromeritics) at liquid nitrogen temperature (–196 °C) using nitrogen as adsorbate. The crystalline phase was analysed by X-ray diffraction measurements. The surface acidities (Lewis and Bronsted) were measured by FTIR PAS technique using pyridine as a probe molecule. It may be noted here that the detail of the acidity measurement procedure is described in our earlier work [8]. These results are reported in Table 1.

2.3. Carbon dioxide TPD

About 0.15 g of calcined sulfated zirconia sample was taken and heated to 450 °C in helium (or air), cooled to room temperature, then carbon dioxide (100% pure) was passed through the catalyst for 30 min. It was heated to 650 °C in helium, and the released CO₂ was analysed in a thermal conductivity detector.

2.4. Butane isomerisation activity study

Time-on-stream (TOS) butane isomerisation study over sulfated zirconia catalyst was carried out in a fixed bed microreactor (SS, i.d.: 8 mm), a schematic representation of the experimental setup is shown in Fig. 1. In a typical experiment, 0.4 g of the catalyst was placed in between the glass-wool beds and was



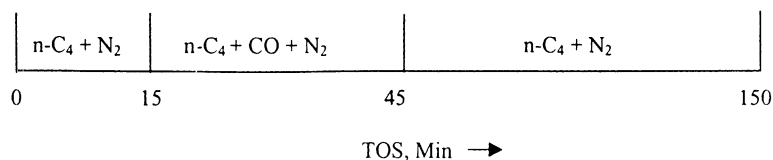
1. 20% n-Butane in nitrogen 2. Carrier 3. Pretreatment 4, 5 & 6. Needle Valves
 7 & 8. Mass flow Meters 9, 10, 11, 12 & 15. Check valves 13. Mixing chamber
 14 & 28. Gas to Fume Hood 16. Furnace temperature controller
 17. Reactor temperature Indicator 18 & 20. Thermocouples
 19. Rubber Septum for Injection 21. Electric Furnace 22. Catalyst
 23. Quartz Wool 24 & 27. Two way valve 25. Bypass Line 26. Glass Sampler

Fig. 1. Schematic representation of the time-on-stream *n*-butane isomerisation setup.

treated at 450 °C under desired gas (nitrogen or air) for 2 h. Then the reactor was cooled to reaction temperature, and depending upon the pretreatment conditions, the reactor was flushed with nitrogen (inert gas) for 15 min to remove any active gaseous components such as oxygen, air etc. from the system. The effect of CO₂ on butane transformation over the catalyst was studied as follows:

Sulfated zirconia catalyst was pre-treated in air, cooled to reaction temperature, flushed with nitrogen for 15 min. A mixture containing butane, CO₂ and nitrogen with a WHSV of 0.45 h⁻¹ (butane:CO₂ volume

ratio at STP = 1:11.6) was passed through the catalyst for a period of 9 h. Then CO₂ in the feed was replaced by nitrogen (keeping WHSV the same as above) and the run was further continued for 1.5 h. This catalyst was heated in air at 450 °C inside the reactor and tested for regenerability using a feed containing butane and nitrogen. Then this catalyst (after regeneration in air) was reacted with a mixture of butane, CO₂ and nitrogen (WHSV, 0.45 h⁻¹) for 2.5 h. It may be noted here that the air used in this study (supplied by Praxair, Canada) contained no CO₂. Products were collected in gas samplers at 5, 10, 15, 20, 30, 45, 60, 90 and



Scheme 1.

150 min of TOS. Hydrocarbons were analysed in a Carle GC in FID mode of operation and fitted with capillary column, whereas an HP GC fitted with a carbosieve column (ss, 2 m long) and operated in TCD mode was used to analyse CO, CO₂, air etc. Details of the analyses are reported in our earlier work [8].

The effect of CO on butane isomerisation activity over sulfated zirconia was studied over the regenerated catalyst varying reaction temperature and butane to CO feed ratio. A schematic representation of the experimental details is shown in Scheme 1.

In a typical experiment, a mixture of *n*-butane and nitrogen was passed through the catalyst for 15 min. At the 15th min a feed containing a mixture of butane, nitrogen and CO (butane:CO volume ratio at STP = 1:11.6) was passed through the catalyst for 45 min, then feed was changed at the 45th minute and another feed containing butane and nitrogen was passed up to 150 min. These experiments were performed at different temperatures in the range 150–300 °C and a WHSV of 0.45 h⁻¹. Experiments were also carried out varying butane to CO feed ratio (Butane:CO volume ratio at STP, 0.085 and 0.15) at a reaction temperature of 200 °C. The feed stream was tested for butene, an impurity often present in butane, and also an active agent that favours coke formation. However, it was found absent within the detection limit of GC.

3. Results and discussion

3.1. Effect of carbon dioxide

Fig. 2 represents the effect of CO₂ on TOS butane isomerisation over a fresh, air-pre-treated sulfated zirconia catalyst at a reaction temperature of 200 °C. It was observed that the catalyst exhibited conversion as high as 2 mol% and the activity did not improve even when CO₂ in the feed was replaced by nitrogen. However, this catalyst on regeneration in air showed

appreciable activity with 24 mol% butane conversion (cf. Fig. 3, pattern 1). It may be noted here, that nitrogen was used as the carrier of butane. This used catalyst on further regeneration in air followed by butane isomerisation study with a mixture containing butane, CO₂ and nitrogen, showed almost similar maximum conversion (22 mol%) as that of the first regenerated catalyst (cf. Fig. 3, pattern 1 and 2). In addition to these, the presence of CO₂ was also found to protect the catalyst from rapid deactivation (cf. Fig. 3, pattern 2).

Effect of carbon dioxide as butane diluent is a less explored area of sulfated zirconia research. Vera et al. [13], in one of their studies on butane isomerisation over sulfated zirconia and related catalysts, have shown the beneficial effect of CO₂. Based on their results they have proposed a redox mechanism for butane isomerisation and argued that electron acceptor molecules such as O₂ and CO₂ promote the oxidation properties of the cations with which they interact. In contrast to their report, in the present investigation we did not see promotional effect (higher conversion) of CO₂ when a mixture of butane, nitrogen and CO₂ was exposed to a fresh, air-pre-treated catalyst (cf. Fig. 2). It may be noted here that a fresh, air-activated sulfated zirconia catalyst, under similar reaction conditions, exhibited butane conversion as high as 37 mol% with nitrogen as butane diluent, and also this catalyst could be fully regenerated on air-pretreatment (cf. Fig. 4).

It has been reported that air activation of sulfated zirconia produces different surface oxy species of zirconium such as O⁻, O₂⁻, O₂²⁻ and O²⁻ [14]. These oxy species, particularly O₂⁻ and O⁻, are highly reactive [15] and basic in nature, and therefore, can combine with CO₂ (an acidic molecule) to form surface adsorbed carbonates. These carbonate species leave the catalyst surface when heated at elevated temperature [16]. So, there is enough possibility that these oxy species might have interacted with CO₂ when exposed to a fresh and air activated sulfated zirconia

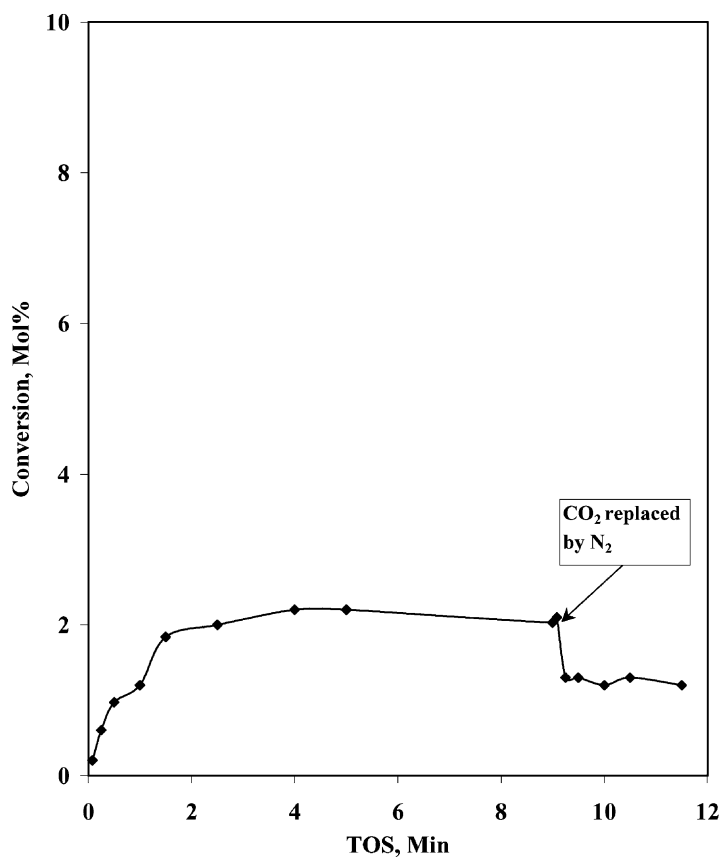


Fig. 2. Effect of carbon dioxide on time-on-stream butane isomerisation at 200 °C over a fresh, air-pre-treated sulfated zirconia catalyst.

catalyst. To support this observation we carried out CO₂ TPD and found that sulfated zirconia catalyst, pre-treated at 450 °C in air prior to CO₂ adsorption, showed three peaks centered at 100, 300 and 570 °C corresponding to CO₂ desorption. On the other hand, catalyst pre-treated in helium showed only two peaks centered at 100 and 400 °C (cf. Fig. 5). The peak at 100 °C is attributed to desorption of the physisorbed CO₂, whereas the peaks at 300, 400 and 570 °C are due to desorption of chemisorbed or chemically modified CO₂. There are reports by Laberty et al. [16] on the oxidation of CO claiming that exposure of an air activated non-stoichiometric nickel manganite spinel to CO could form CO₂, which on further interaction with the oxy species on catalyst could generate species such as CO₂⁻, CO₃²⁻ (ads) and HCO₃²⁻. Formation of CO₂⁻ species has recently been demonstrated by Kohno et al. [17] during their studies on

photoreduction of CO₂ with hydrogen over zirconia. All these reports in conjunction with our observations in this work suggest that CO₂ interacts with the surface oxy species of sulfated zirconia. It could also be a possibility that water in the catalyst interacts with CO₂ poisoning the catalyst. Gonzalez et al. [18] performed butane isomerisation over sulfated zirconia by injecting different amounts of water onto the catalyst. They observed the catalyst pre-treated at 500 °C when dosed with 75 μl of water at 150 °C showed improved activity. However, in the present study the catalyst was pre-treated in situ at 450 °C for 2 h and cooled to 200 °C to study the effect of CO₂ on butane isomerisation. Pretreatment of the catalyst at such a high temperature for 2 h is believed to remove all moisture from the catalyst surface. Therefore, we discard the possibility that CO₂ poisoned the fresh, air pre-treated catalyst by interfering with the water on catalyst surface.

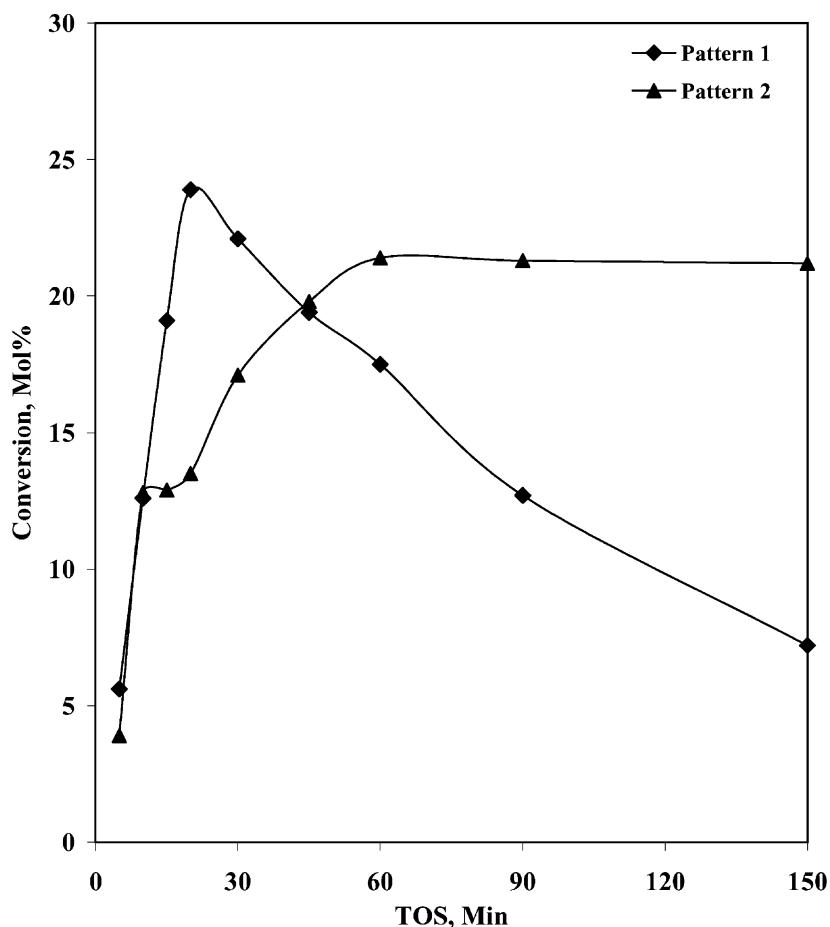


Fig. 3. Butane isomerisation over air-regenerated sulfated zirconia, at 200 °C, as a function of time-on-stream. Pattern 1: isomerisation studied with a feed containing nitrogen and *n*-butane and pattern 2: isomerisation studied with a feed containing *n*-butane, CO₂ and nitrogen.

Moro-Oka [15] claimed the nucleophilic oxy species, which are also strong bases, can abstract hydrogen from saturated hydrocarbons. In oxidative coupling of methane, it was proposed that nucleophilic oxy species have the capacity to abstract hydrogen from methane [19]. It is known that acidity of *n*-butane is more than methane and, therefore, can easily be dehydrogenated by these strongly basic, nucleophilic oxy species. In fact, it was reported that butane isomerisation activity over an air-activated sulfated zirconia catalyst is more than that activated in nitrogen or helium. Moreover, sulfated zirconia is active for butane isomerisation at or <100 °C only when pre-treated in air [20]. Based on these reports and our result on the effect of CO₂, we propose that exposure

of a freshly-air-activated sulfated zirconia to a mixture containing butane and CO₂ led to competitive adsorption of both species on the catalyst surface. Some of the active oxygen species might have dehydrogenated butane. However, since butane content in the feed stream was much less as compared to CO₂ (butane:CO₂ mole ratio = 1:11.6) most of the oxy species might have reacted with CO₂ thereby forming, most probably, the surface adsorbed carbonates. This fact, that surface oxy species reacted with CO₂ forming most likely carbonate species, is further confirmed when the activity of sulfated zirconia did not improve after replacing CO₂ with nitrogen in the feed (cf. Fig. 2).

Laberty et al. [16] have claimed that hydrogen carbonate species i.e. HCO₃²⁻ were formed rapidly by

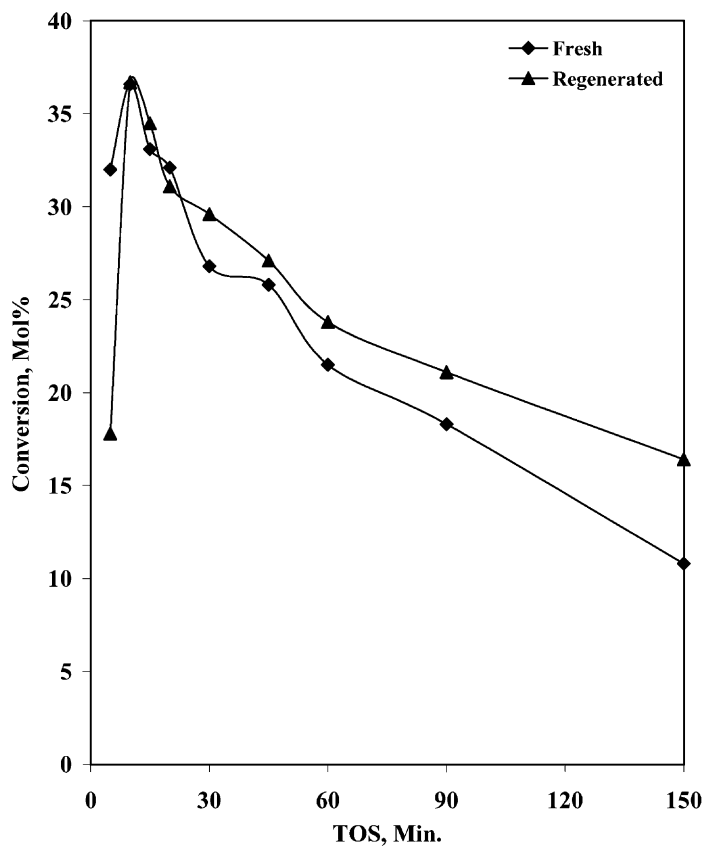


Fig. 4. Butane isomerisation over a fresh, air pre-treated and a use air-regenerated sulfated zirconia at 200 °C at a WHSV of 0.45 h⁻¹.

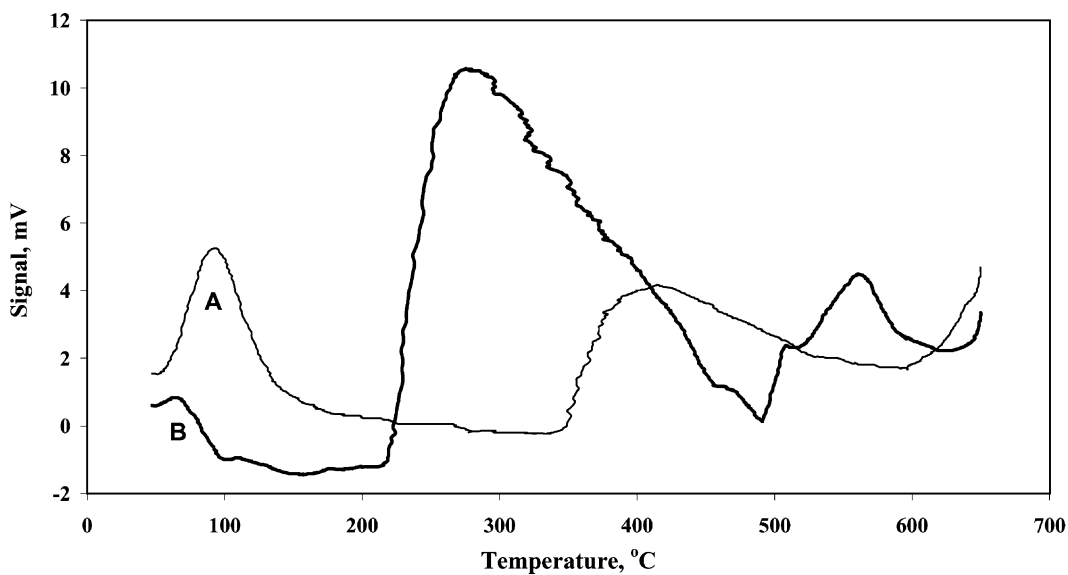


Fig. 5. Effect of pretreatment gases on the CO₂ TPD patterns of sulfated zirconia calcined at 600 °C (A) helium; (B) air.

the reaction of OH^- group with the acidic CO_2 and were easily removed when outgased. The carbonate species that were progressively accumulated on the catalyst surface were formed at the expense of the hydrogen carbonates, and were only partly and slowly decomposed upon outgasing. Aiken et al. [21] reported that among the anions such as sulfate, hydroxyl and carbonate, sulfate is most stable and carbonate is least stable on zirconia surface. Therefore, decomposition of carbonate or bicarbonate species at low temperature such as 450°C seems possible, as the surface adsorbed species are not exactly zirconium carbonate or bicarbonate. The higher activity of the air-regenerated catalyst (cf. Fig. 3, pattern 2) compared to the fresh one (cf. Fig. 2) suggests that surface carbonates or bicarbonates are decomposed during air activation (also cf. Fig. 5, pattern B). It may be noted here that the catalyst activity was never zero, whether CO_2 was exposed to a fresh, an air-activated catalyst, or a regenerated catalyst. This observation in conjunction with the report by Hong et al. [9], who claimed that lattice oxygen of sulfated zirconia could act as an active site, suggests surface carbonates are formed by the interaction of adsorbed oxygen on sulfated zirconia surfaces. However, the interaction of lattice oxygen of zirconia with carbon dioxide cannot be ruled out.

It is evident that surface oxygen, generated by air pretreatment of sulfated zirconia, is the major cause of catalyst poisoning by CO_2 (cf. Fig. 2). However, one can ask that if this is true then why does an air-regenerated sulfated zirconia show no such effect in the presence of CO_2 , rather it showed a beneficial effect on the activity of sulfated zirconia (cf. Fig. 3, pattern 2). To explain this we propose that air activation of the CO_2 poisoned sulfated zirconia could not regenerate all the active sites. This is in accordance with the CO_2 TPD result (cf. Fig. 5, pattern B) and that of the report of Laberty et al. [16] that the surface carbonates are partly decomposed on heating the used catalyst. In fact, the above proposition is supported by the observation that a regenerated sulfated zirconia showed significantly lower conversions in the presence of CO_2 and nitrogen as butane diluents (cf. Fig. 3) than a fresh, air-pre-treated catalyst (cf. Fig. 4).

The slow deactivation of the catalyst in the presence of CO_2 could be because of interaction of the deactivation sites with CO_2 prohibiting the reacting intermediates (such as C_8^+ species [8]) from coke formation.

In our earlier report [8] we have shown that catalyst deactivation is very fast ($\sim 90\%$ decrease in 15 min of TOS) in the presence of air as a butane diluent. This implies oxygen in the feed promotes catalyst deactivation. Probably, the surface oxy species are also the cause of catalyst deactivation. However, it is difficult at this point to explain the nature of interaction between CO_2 and these oxy sites prohibiting catalyst deactivation.

3.2. Effect of carbon monoxide

Effects of CO on butane isomerisation over regenerated sulfated zirconia catalyst are shown in Fig. 6. It is observed that the introduction of CO into the feed stream during the reaction drastically reduced butane conversion over an air regenerated sulfated zirconia catalyst. On removal of CO from the feed the catalyst regained its activity, almost immediately. In addition, butane conversion, even in presence of CO (during the TOS of (15–45 min), increased with increase in reaction temperature from 150 to 300°C .

During their investigations, Wan et al. [10] found CO irreversibly destroyed the catalytic active sites of iron–manganese promoted sulfated zirconia. In their study the catalyst was activated in situ at 650°C in air and *n*-butane reaction was carried out at 30°C . Pure CO was introduced into the reaction system during the rising activity period. During this process, they observed rapid decline in the butane conversion, and eventually fell to zero within 1 min of TOS. Not only that, the catalyst activity could not be recovered even when the CO from the feed was withdrawn, and calcining the catalyst at 200°C in helium. Moreover, the catalyst showed activity and rapid deactivation when the reaction temperature was increased to 200°C . The near room temperature activity of the catalyst was regained only by activating it in air at 650°C . Also, a gas chromatographic analysis of the reaction products showed evolution of CO_2 . Based on these observations they concluded that CO was oxidised to CO_2 by the oxy species of the catalyst. To confirm the oxidation of CO was not by the oxygen coming out of disproportionation of CO, they also analysed the carbon content in the CO exposed catalyst and found no carbon deposition confirming that CO is oxidised using the labile active oxy species. Based on these findings, Wan et al. proposed that the low

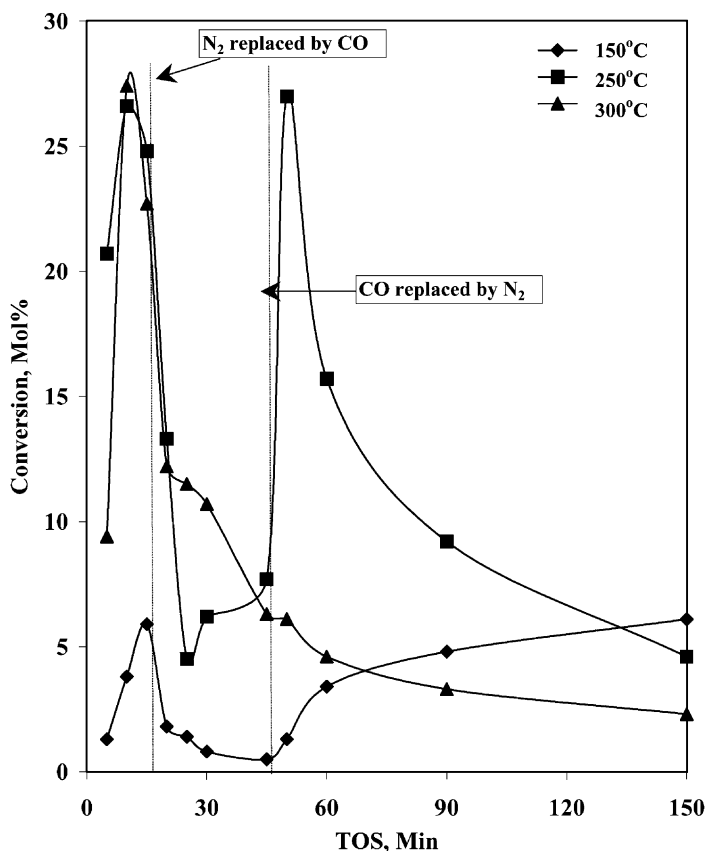


Fig. 6. Effect of CO on time-on-stream butane isomerisation over an air-regenerated sulfated zirconia catalyst at different temperatures.

temperature active sites are the iron-oxy species, which are destroyed during CO exposure. In another study, Morterra et al. [11] reported the effect of CO on butane isomerisation at 50 °C on promoted sulfated zirconia in which they introduced CO during the deactivation period. They observed CO reversibly poisons the catalyst. This observation was attributed to interaction of CO molecules with the Lewis acid sites in the catalyst. They also proposed that Lewis acid sites are the active sites for butane isomerisation.

On the other hand, Adeeva et al. [22] performed butane isomerisation in the presence of CO over sulfated and iron manganese promoted sulfated zirconias at 150 and 80 °C, respectively, and observed that CO reversibly poisoned both catalysts. Moreover, sulfated zirconia catalyst regains its activity immediately after the withdrawal of CO from the feed, whereas iron manganese promoted sulfated zirconia took a long

time to recover its activity. Also, CO suppresses the rate of butane isomerisation even when it was not adsorbed on Lewis acid sites. Based on these observations and an earlier report by Sommer et al. [23], Adeeva et al. proposed that CO forms oxocarbenium ion with butane. And the stability of the oxocarbenium ion on the catalyst surface determines the rate at which the activity recovers. In the present investigation, CO was introduced during the rising in catalyst activity (cf. Fig. 6), and by the time CO was introduced the labile or reactive oxy species of zirconium might have participated in butane activation. Therefore, the oxidation of CO, if it is at all a possibility, by the labile or active surface oxy species, might not be a case causing reversible poisoning. In a recent report, it was proposed that butane isomerisation reaction over sulfated zirconia proceeds via a chain mechanism consisting of initiation, propagation and termination

[9]. Since the activity of the catalyst was never zero in any case of CO poisoning it is clear that initiation sites are probably not blocked or deactivated by CO. Had it been the case, the CO exposed catalyst would have not regained activity so quickly after the feed was freed from CO. So, the most probable process that seems to be affected is the chain propagation. Assuming carbonylation of reacting intermediate (the $C_8H_{19}^+$ ion) as one of the processes in the presence of CO one can write the following:



In liquid super acid media CO was used to quench the carbocation to prohibit oligomerisation [24]. In the present case, if the carbocation reacts with CO

to form oxocarbenium ion and gets stabilised on the catalyst surface, then obviously the rate of butane isomerisation will be suppressed because of the competition between the above two equilibrium processes. In fact, the carbonylation of the reacting intermediate has been recently confirmed by Luzgin et al. [25] who performed in situ MAS NMR measurements to study pentane isomerisation over sulfated zirconia both in the absence and presence of CO, and observed the formation of aldehydes and ketones (Koch products) from pentane in the presence of CO. These reports along with our observations on the effect of CO on *n*-butane isomerisation indicate that carbonylation is a dominant phenomenon when CO is present in the butane stream. Increase in the reaction temperature increased the conversion level of butane in the presence of CO, and at 300 °C the effect of CO seems absent. These observations suggest that the equilibrium

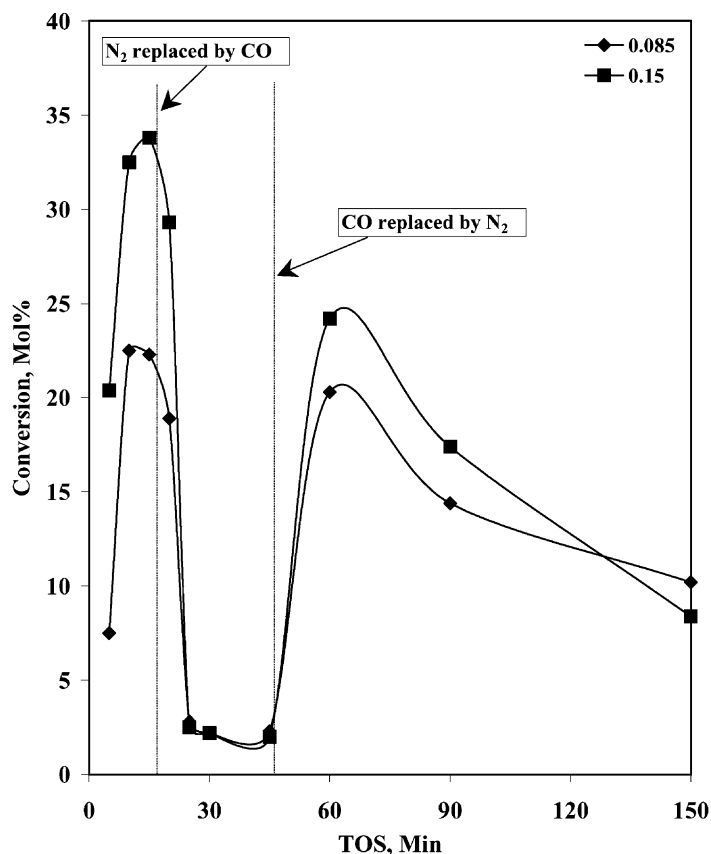


Fig. 7. Effect of *n*-butane to CO ratio in the feed on *n*-butane isomerisation at 200 °C over an air-regenerated sulfated zirconia.

showed in Eq. (1) shifted to the decarbonylation side favouring C_8^+ to undergo isomerisation. At 300 °C, the butane conversion pattern (cf. Fig. 6) indicates that CO adspecies (oxocarbenium ion) probably did not form at such a high temperature. Moreover, at that temperature cracking is dominant over isomerisation. Therefore, by the time CO was withdrawn from the feed stream most of the initiation sites were deactivated either via coke formation or reduction. Therefore, even when CO was withdrawn from the feed the conversion did not improve.

Effect of CO concentration on conversion of butane over sulfated zirconia catalyst was also tested and the results are shown in Fig. 7. It is seen, that the extent of decrease in activity of sulfated zirconia is the same irrespective of CO concentration. Sommer et al. [26], in one of their studies on isobutane isomerisation over deuterated β -zeolite catalyst, found that the concentration of CO in the feed was very crucial in CO poisoning. They observed that a large excess (>90%) of CO is necessary to completely poison the catalyst, and the activity can be reduced by 80% with a CO concentration of 20% in the (CO + N₂) mixture in the feed. In the present investigation, CO concentration (with respect to N₂) was in the range 35–75%. This region of CO concentration, as observed by Sommer et al. [26], is a region where the poisoning effect of CO did not change much. This is probably the reason for the observed activity with changing CO concentration in the feed stream (cf. Fig. 7). This observation also indicates that the CO poisoning mechanism is the same in the case of *n*-butane and isobutane isomerisations, and independent of catalyst type. In addition, the observation also indicates that CO concentration, and consequently the oxocarbenium ion, strongly influences the propagation step in butane *n*-butane isomerisation.

4. Conclusions

Based on the results, it is concluded that surface oxy species present on sulfated zirconia, generated by air pretreatment, play an important role in butane isomerisation. The effect of CO₂ on butane isomerisation indicates an acid-base type of interaction existing between the catalyst surface and CO₂. The extent of interaction, i.e. strong or weak, probably depends on the type of oxy species present on the catalyst surface.

The reversible poisoning effect of CO suggests that CO probably involves in forming surface adspecies, which are in dynamic equilibrium with the gas phase CO, influencing chain process of the three-step chain mechanism of butane isomerisation.

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