

Role of acidic and basic sites of Al_2O_3 in predicting the reaction pathway of isophorone transformation

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Abstract

Masking of either acidic or basic sites of aluminum oxide, by co-feeding of NH_3 or CO_2 , respectively, along with isophorone, indicate the involvement of weak/moderate basic sites to abstract a proton to form an enolate ion followed by involvement of weak/moderate acid sites for dienone–phenol rearrangement to yield aromatization products and involvement of strong acidic sites for yielding decomposition products. © 2004 Elsevier B.V. All rights reserved.

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1. Introduction

Aromatization of isophorone to 3,5-dimethyl phenol is an important reaction in view of its wide industrial applications. 3,5-Dimethyl phenol is used as a disinfectant and as a starting material for the preparation of resins, Vitamin E and other chemicals like dyes, agrochemicals, pharmaceuticals and aroma chemicals [1–4]. 3,5-Dimethyl phenol can be synthesized by hydroxylation of xylenes and/or alkylation of phenols, but the selectivity to the desired product is very poor due to *ortho* and *para* directing nature of hydroxyl and alkyl groups, respectively. Because of many disadvantages of these processes like low yields, low selectivities and large amount of by-product formation, catalytic aromatization of isophorone has been recognized to be a promising, economically viable and environmentally benign alternative route for the synthesis of 3,5-dimethyl phenol.

With the exception of few reports, the data on this catalytic transformation of isophorone is mainly patented [1–3,5]. Our previous results on the application of carbon

covered alumina (CCA), $\text{Cr}_2\text{O}_3/\text{SiO}_2$, $\text{K}_2\text{O}-\text{Cr}_2\text{O}_3/\text{Al}_2\text{O}_3$ and $\text{K}_2\text{O}-\text{Cr}_2\text{O}_3/\text{CCA}$, as catalysts reveal the formation of several products, through series–parallel steps, particularly aromatization, decomposition and cross-condensation when isophorone is contacted in the vapor phase with these catalysts [6–9]. Unambiguously, the selective production of 3,5-dimethyl phenol is a challenging task. The formation of various products when isophorone is contacted with the catalyst depends on the strength and number of acidic and basic sites present on the catalyst surface. So far, no in-depth study has been reported on the involvement of acidic and basic sites in the conversion of isophorone. The present study is aimed in this direction. For this purpose two kinds of Al_2O_3 samples with variable acidic and basic sites are selected and an attempt is made to find out the effect of these sites in the reaction pathway leading to various products.

2. Experimental

Two kinds of commercial Al_2O_3 samples obtained from M/S. Qualigens Fine Chemicals, India, M/S. Loba Chemie

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Ltd., India have been designated as Al-1 and Al-2, respectively, and are selected for characterization and activity study. The XRD analysis of these samples revealed that they are in γ -phase. Surface areas of these samples were determined on an all glass high vacuum unit capable of attaining 10^{-6} Torr, by standard BET method with N_2 as adsorbate. Pulse chemisorption followed by temperature programmed desorption (TPD) of NH_3 is employed to evaluate acid site distribution of the catalysts. Prior to the TPD experiment, NH_3 from 10% NH_3 in He mixture has been adsorbed on pretreated catalyst (pretreatment has been performed by passing He at 723 K for 2 h and then cooling to room temperature) at room temperature in pulses through a six-port valve. In a typical experiment, about 200 mg of the catalyst sample is placed in a micro-reactor of 3 mm i.d., and 250 mm long quartz reactor and pretreated at 723 K for 2 h in He flow. The outlet of the reactor is connected to a micro-thermal conductivity detector (TCD) equipped GC-MS (QP-5050, supplied by M/S. Shimadzu Instruments, Japan) through a blank column. After the pretreatment of the catalyst, pulses of 10% NH_3 in He are injected at room temperature through a 500 μ l loop connected to the six-port valve until no further change in the intensity of the outlet NH_3 (monitored by a data station with CLASS 500 GC software) is observed. After the completion of the pulse chemisorption, the reactor temperature is maintained at 373 K in He flow for 2 h to remove the physisorbed NH_3 . The temperature is then increased linearly at a programmed rate of 5 K min^{-1} from 373 to 1073 K where 30 min isothermal conditions are maintained, followed by cooling to room temperature. The desorption patterns are monitored through a GC software, for signals coming out of TCD. The basic site distributions are measured by pulse chemisorption of CO_2 using 10% CO_2 in He through a six-port valve followed by TPD of CO_2 in a similar manner, as described above.

Reaction of isophorone was performed in a fixed-bed tubular reactor (10 mm i.d., 300 mm long quartz reactor) using 1 g catalyst at atmospheric pressure, different temperatures ranging from 673 to 793 K at a WHSV = 1 h^{-1} and proper care has been taken to overcome the diffusion limits. Experiments with quartz pieces in place of catalyst did not give any observable isophorone conversion ruling out the possibility of homogeneous surface/volume effect. Prior to catalytic tests, the catalyst was pretreated in situ in air at 793 K for 1 h in order to remove H_2O and CO_2 . The product mixture was collected in regular intervals (for every 1 h) after the steady state was achieved (~ 30 min) at each reaction temperature. The analysis of the products was carried out on a GC-MS (QP-5050 supplied by M/S. Shimadzu Instruments) with EI-mass detector using DB-5 capillary column (0.32 mm diameter and 25 m long supplied by M/S. J & W Scientific Instruments, USA). The main reaction products were 3,5-dimethyl phenol, 2,3,5-trimethyl phenol, *m*-cresol, mesitylene, phorone isomers, diacetone alcohol and mesityl oxide. Traces of isoxyletones and some un-identified products were also observed, in some cases.

3. Results and discussion

The pulse chemisorption data of CO_2 and NH_3 at room temperature provides the total amount of respective gases chemisorbed on each catalyst. Table 1 shows the BET surface area and NH_3 and CO_2 uptakes. From Table 1, it is clear that the BET surface area of Al-2 is somewhat more than that of Al-1. While Al-2 possesses lower number of acidic sites, Al-1 possesses lower number of basic sites.

Fig. 1 shows the CO_2 TPD patterns. CO_2 TPD pattern of Al-1 indicates the presence of moderate basic sites with major population at $T_{max} = 700$ K and strong basic sites T_{max} beyond 900 K are not as many as those of moderate sites. Presence of weak basic sites on Al-1 can also be seen from its CO_2 TPD pattern ($T_{max} = 400$ K). Presence of strong basic sites ($T_{max} = 900$ K) can be seen from the CO_2 TPD pattern of Al-2.

Fig. 2 shows the NH_3 TPD patterns of Al-1 and Al-2. NH_3 TPD pattern of Al-1 shows two desorption maxima, one a high intense signal at $T_{max} = 875$ K which is attributed to the presence of strong acidic sites and the other, a low intense signal at $T_{max} = 400$ K indicating the presence of weak acidic sites. The TPD pattern of Al-2 indicates the presence of mainly strong acidic sites due to the desorption signal at T_{max} of 900 K.

Our previous studies revealed the enhancement of selectivity towards aromatization products upon carbon coverage on Al_2O_3 which was attributed to the decrease in the strong

Table 1
BET surface area and uptakes of CO_2 and NH_3

| S. no. | Catalyst code | BET surface area ($m^2 g^{-1}$) | CO_2 uptake ($\mu mol g^{-1}$) | NH_3 uptake ($\mu mol g^{-1}$) |
|--------|---------------|-----------------------------------|------------------------------------|------------------------------------|
| 1 | Al-1 | 58.5 | 56.6 | 55.6 |
| 2 | Al-2 | 67 | 68.7 | 43.6 |

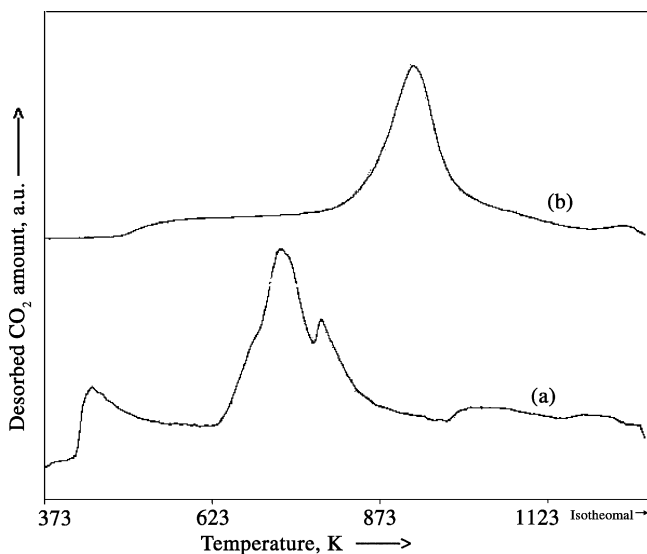


Fig. 1. CO_2 TPD patterns of aluminas: (a) Al-1 and (b) Al-2.

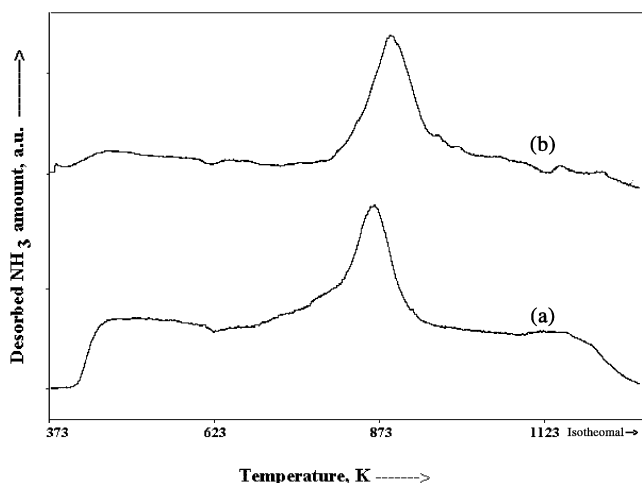


Fig. 2. NH_3 TPD patterns of aluminas: (a) Al-1 and (b) Al-2.

acidity of the catalyst [6]. Another study of ours reveals the enhancement of aromatization selectivity upon addition of K_2O to $\text{Cr}_2\text{O}_3/\text{Al}_2\text{O}_3$ and $\text{Cr}_2\text{O}_3/\text{carbon covered alumina (CCA)}$ which was ascribed to the increase in coordinatively unsaturated sites of Cr_2O_3 [9]. These studies clearly indicate that strong acidic sites favor the formation of decomposition products.

Fig. 3 shows that even though the isophorone conversion is same on both the catalysts at low temperatures (at a reaction temperature of 673 K), Al-1 exhibit higher conversion at 753 K than Al-2. It was earlier reported that coke formation starts on Al_2O_3 during isophorone conversion, at a reaction temperature of ≥ 753 K [6]. It was also reported that at and above this temperature, the conversion remains the same [6]. Hence the reaction temperature of 753 K has been chosen as optimum and the catalytic activities of the two catalysts were compared at 753 K. At 753 K, the decomposition products were minimum over Al-1 (Fig. 3). Al-2 possesses strong acidic sites while Al-1 possesses strong and weak acidic sites. The total number of acidic sites are in the following order: Al-2 > Al-1. One can thus infer that strong acid sites promote the formation of decomposition products.

The number of basic sites are more on Al-2 which are mostly strong in nature. On the other hand, Al-1 catalyst possesses mainly moderate basic sites. Al-1 catalyst exhibits higher selectivity towards aromatization products at 753 K (Fig. 3). This clearly indicates that moderate basic sites are responsible for the formation of aromatization products.

Transformation of isophorone is a complex reaction network; hence numerous products are possible depending on both the catalyst and the operative conditions employed. Under similar reaction conditions the product distribution of isophorone transformations were found to be different over the two catalysts studied (Table 2) which may be ascribed to the differences in the acidic/basic site distribution.

Based on literature [4,6–10] and the present results, the following mechanism (Scheme 1a) is proposed for the aromatization of isophorone to 3,5-dimethyl phenol on basic/acidic

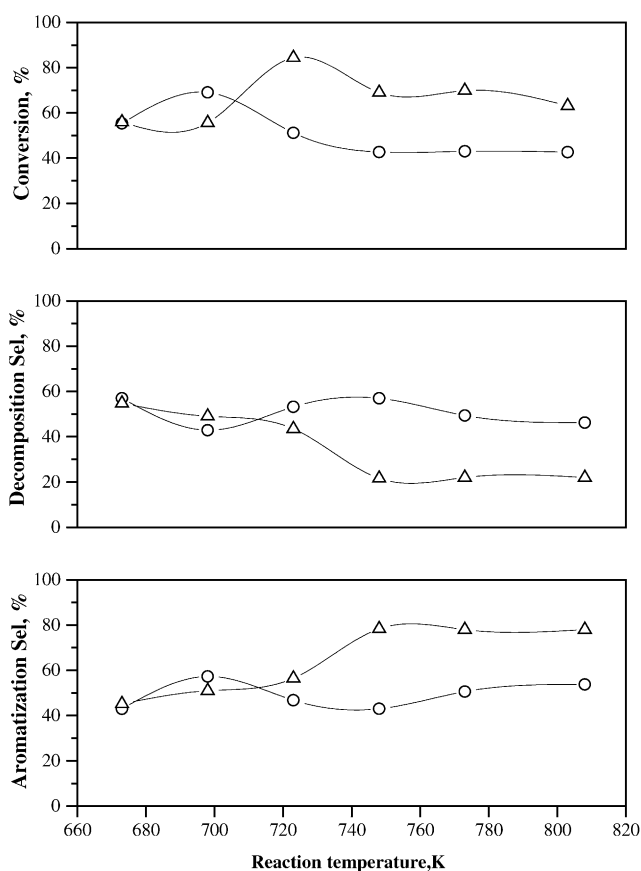
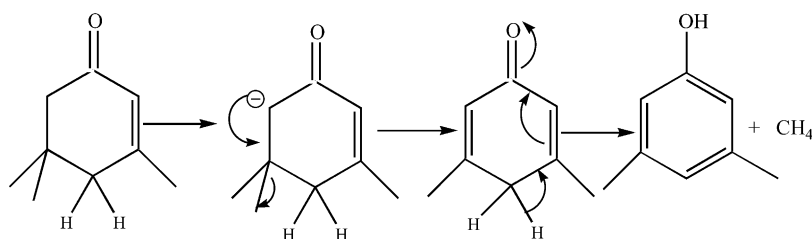


Fig. 3. Effect of reaction temperature on the activity of aluminas (Δ) Al-1 and (\circ) Al-2.

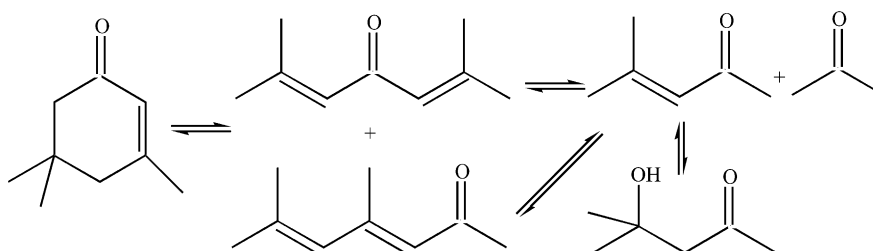
sites of Al_2O_3 . Initially, the basic sites of Al_2O_3 abstract the proton adjacent to the carbonyl carbon and generate the enolate anion of isophorone which in turn gets demethylated and dienone–phenol rearrangement takes place on acidic site of weak/moderate acidic strength for the formation of 3,5-dimethyl phenol and finally, the proton recapture takes place from the protonated basic sites of Al_2O_3 leading to the formation of CH_4 (Scheme 1a). Formation of other aromatization

Table 2
Reaction product distribution at a reaction temperature of 753 K

| Product distribution | Product components (%) | |
|------------------------|------------------------|------|
| | Al-1 | Al-2 |
| Unreacted isophorone | 31.0 | 57.3 |
| Aromatization products | | |
| 3,5-Xylenol | 38.5 | 14.6 |
| 2,3,5-Trimethyl phenol | 6.0 | 3.7 |
| <i>m</i> -Cresol | 9.5 | 0 |
| Total | 54.0 | 18.3 |
| Decomposition products | | |
| Mesityl oxide | 2.3 | 2.5 |
| Diacetone alcohol | 0 | 0.5 |
| Trimethyl benzenes | 2.2 | 2.6 |
| Phorone isomers | 10.5 | 18.8 |
| Total | 15.0 | 24.4 |



Scheme 1. Reaction pathway leading to (a) 3,5-dimethyl phenol and (b) other aromatization products.



Scheme 2. (a) Isophorone decomposition into phorone and 4,6-dimethyl hepta-3,5-diene-2-one. (b) Diacetone alcohol decomposition into isobutene and acetic acid.

products have been shown in Scheme 1b. These products are formed due to transalkylation of 3,5-dimethyl phenol.

Aromatization of isophorone to 3,5-dimethyl phenol is favorable on Al-1 than on Al-2. Availability of more number of moderate basic sites on Al-1 is one of the reasons, for the generation of enolate ion of isophorone in the first step to yield 3,5-dimethyl phenol. The data on TPD of CO_2 correlates the activity results of Al-1 and Al-2 catalysts.

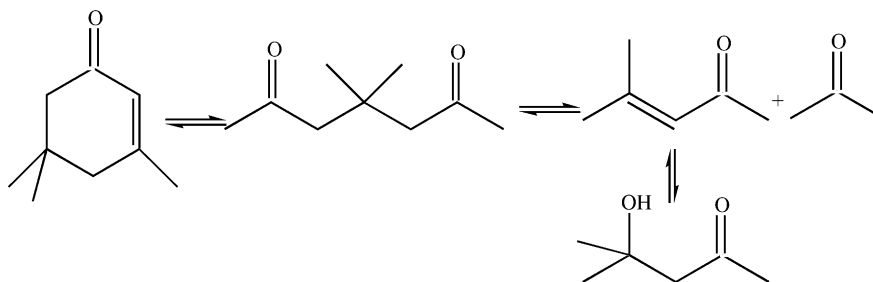
In the presence of acidic sites on Al_2O_3 , isophorone decomposes into phorone and 4,6-dimethyl hepta-3,5-diene-2-one by intra-molecular retro-Michael condensation. These two decomposition products further converted into mesityl oxide and acetone, diacetone alcohol, isobutene and acetic acid as shown in Scheme 2a and b [5].

The decomposition of isophorone into different products on Al-2 is higher than on Al-1. Isophorone may also be decomposed into 4,4-dimethyl hepta-2,6-dione by intra-molecular retro-aldol condensation on acidic sites which may be further converted into mesityl oxide, acetone, diacetone alcohol, isobutene and acetic acid as shown in Scheme 3 [5].

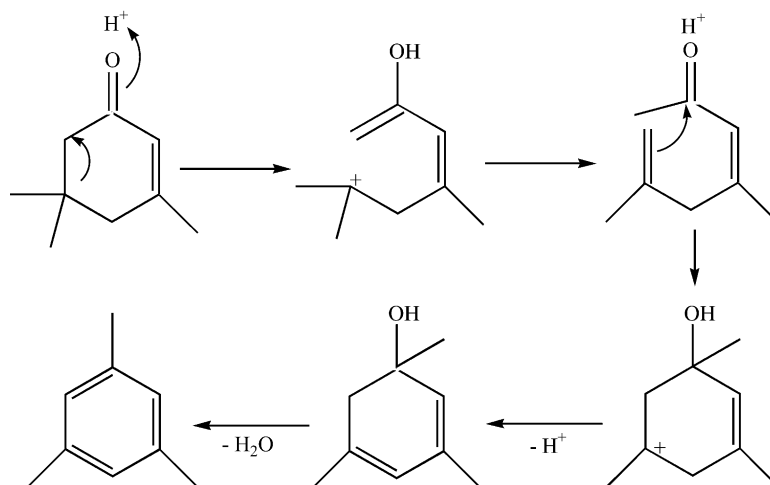
The mesitylene formation occurs from isophorone and 4,6-dimethyl hepta-3,5-diene-2-one. Isophorone on acidic

sites is converted into mesitylene as shown in Scheme 4 [11]. The 4,6-dimethyl hepta-3,5-diene-2-one, the decomposition product of isophorone on basic sites gets converted into mesitylene by the abstraction of proton from the terminal methyl group and intra-molecular 1,6 aldol condensation followed by dehydration (Scheme 5) [11–13].

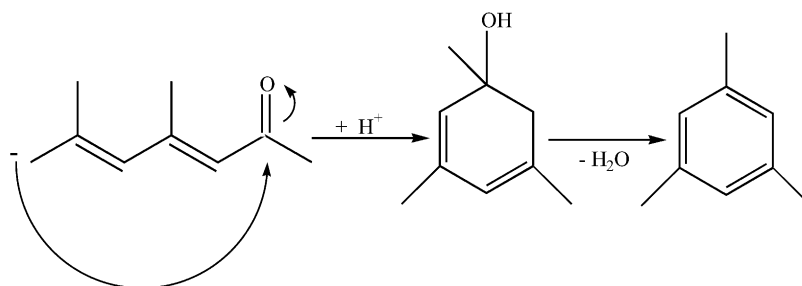
Among the aromatization products of the reaction, 3,5-dimethyl phenol is the major product. In order to test the reaction mechanism, separate reaction runs using (i) co-feeding of CO_2 along with isophorone and (ii) co-feeding of NH_3 over Al-1 catalyst has been performed and the results are shown in Fig. 4. When only N_2 is maintained along with isophorone, the conversion of isophorone is 68% with selectivities towards decomposition and aromatization products are 22 and 78%, respectively. When CO_2 is maintained as co-feed, the conversion of isophorone is dropped down to 54% with selectivity towards decomposition products is enhanced to 44%. As a result, the selectivity towards aromatization products are dropped to 55%. Upon the addition of CO_2 to the feed mixture, the overall activity of the catalyst is diminished which is an indication that basic sites (strong and some of the moderate sites) of the catalysts are poisoned. Fig. 1 indicates the



Scheme 3. Isophorone decomposition to 4,4-dimethyl hepta-2,6-dione.



Scheme 4. Isophorone rearrangement to mesitylene.



Scheme 5. Rearrangement of 4,6-dimethyl hepta-3,5-diene-2-one to mesitylene.

presence of moderate sites in the temperature region between 673 and 900 K. It is worthwhile to note that the initiation of aromatization path way needs basic sites of Al_2O_3 . It is reported that the adsorption of CO_2 easily blocks O^{2-} type of basic site of the catalyst unaffected the OH^- type of basic sites. The O^{2-} type of basic sites abstract an H^+ from

the reactant to produce anionic intermediates in the reactions [14–21]. Considerable inhibition of aromatization activity by the chemisorption of CO_2 indicates that the active sites for aromatization of isophorone to 3,5-dimethyl phenol are O^{2-} type of basic sites.

The co-feeding of NH_3 with reaction mixture results in the decrease of the overall catalytic activity of the catalyst (conversion of isophorone is dropped to 52% and the aromatization selectivity is enhanced to 89%). Inhibition of strong acidic sites of Al_2O_3 catalysts is known upon addition of NH_3 . The activity data provide the information that both decomposition and aromatization pathways of isophorone transformations require certain number of acidic sites. It is clear that the ammonia addition to the catalyst suppress the strong acid sites, which can lead to the suppression of decomposition products (from 22% to 11%). Thus NH_3 co-feeding helps to increase the selectivity towards aromatization products (from 78% to 89%). The reaction temperature of 753 K is sufficient to remove the adsorbed NH_3 from the weak acidic centers (during the activity run where NH_3 co-feeding was maintained) and these weak acidic centers are responsible for the dienone–phenol arrangement. This appears to be the reason why aromatization of isophorone to 3,5-dimethyl phenol has been substantially increased when NH_3 is maintained as a co-feed.

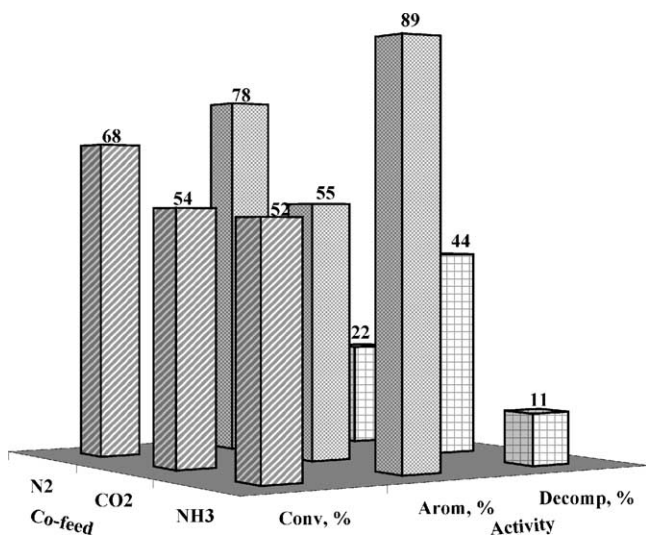


Fig. 4. Effect of CO_2 and NH_3 as co-feed along with isophorone on the activity of Al-1 (reaction temperature = 748 K).

4. Conclusions

The pulse chemisorption of CO₂ and NH₃, followed by TPD of CO₂ and NH₃, respectively, on Al-1 and Al-2 catalysts and the co-feeding studies of CO₂ and NH₃ along with isophorone during reaction on Al-1 catalyst, clearly indicates that aromatization of isophorone requires both moderate/weak basic sites in the first step to generate enolate ion. In the second step, moderate/weak acidic sites are needed for the dienone–phenol rearrangement. Decomposition of isophorone pathway proceeds only on moderate/strong acidic sites.

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