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n-pentane isomerization and disproportionation catalyzed by promoted and unpromoted sulfated zirconia

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Isomerization and disproportionation of n-pentane were catalyzed by sulfated zirconia, Fe- and Mn-promoted sulfated zirconia, and Pt-, Fe-, and Mn-promoted sulfated zirconia in a flow reactor at temperatures of -25 to 50 °C and n-pentane partial pressures of 0.005–0.01 atm. Incorporation of the Fe and Mn promoters increased the activity of the sulfated zirconia by two orders of magnitude at 50 °C; addition of Pt to the latter catalyst increased the activity only slightly. The primary reactions, disproportionation (to give butanes and hexanes) and isomerization, occurred in parallel; secondary disproportionation reactions gave heptanes, propane, butanes, and pentanes. The data are consistent with acid–base catalysis and carbenium ion intermediates, and the isomerization is inferred to proceed both by unimolecular and bimolecular mechanisms. H_2 in the feed stream and Pt in the catalyst both led to reductions in the rate of catalyst deactivation.

Keywords: n-pentane, isomerization, sulfated zirconia, iron- and manganese-promoted sulfated zirconia, isomerization of n-pentane, disproportionation of n-pentane

1. Introduction

Low temperatures are advantageous for alkane isomerization because the equilibria favor branched (high-octane-number) products. Typical alkane isomerization catalysts are acids, and the only ones active at low temperatures are extremely strong acids. For example, $AlCl_3$ supported on alumina has long been applied in isomerization processes, but its corrosiveness and potential for pollution make it increasingly less acceptable in practice.

More stable and potentially useful solid acid catalysts than supported $AlCl_3$ have been made by sulfation of metal oxides such as zirconia [1–3]. An advance in this class of catalyst was described by Hsu et al. [4–9], who reported [4] Fe- and Mn-promoted sulfated zirconia (FMSZ) catalysts that are active for n-butane isomerization even at room temperature; the promoter effect has been confirmed by several groups [10–14]. The results suggest that the catalyst might be useful for isomerization of other light alkanes, and our goal was to evaluate its performance for conversion of n-pentane. Following a preliminary report [15], we present data indicating the effects of Fe and Mn as well as Pt promoters of sulfated zirconia (SZ) and evidence of the reaction network (involving isomerization and disproportionation) and reaction mechanism (involving both monomolecular and bimolecular reactions of carbenium ions).

2. Experimental

The methods were as described elsewhere [15]. The catalysts included (a) unpromoted SZ (1.8 wt% S); (b) FMSZ containing 1.5 wt% Fe, 0.5 wt% Mn, and 1.8 wt% S; and (c) PtFMSZ containing 1.5 wt% Fe, 0.5 wt% Mn, 1.8 wt% S, and 0.2 wt% Pt, prepared from dried, uncalcined Fe- and Mn-promoted sulfated zirconium hydroxide by addition of H_2PtCl_6 by incipient wetness followed by drying at 120 °C for 24 h and calcination at 650 °C for 3 h. Before each catalysis experiment, the catalyst in flowing N_2 (30 ml (NTP)/min) was heated from 20 to 450 °C at a rate of 7.1 °C/min, and the temperature was then held at 450 °C for 1.5 h; then the catalyst was cooled to the reaction temperature in N_2 flowing at 30 ml/min. The catalyst mass varied from 0.1 to 1 g. Reactions were conducted at 1 atm in a temperature-controlled stainless-steel reactor. The partial pressure of n-pentane in the reactant stream was 0.01 atm in most experiments and sometimes 0.005 atm. The space velocity varied between 0.0192 and 0.192 g of pentane/(g of catalyst × h). Products were analyzed by gas chromatography.

3. Results

3.1. Reaction products

Conversion of n-pentane in the presence of each catalyst gave the following products at -25 and 0 °C: isobutane, isopentane, and traces of 2-methylpentane (2MP) and 3-methylpentane (3MP); these products and small amounts of hexanes and n-butane with traces of propane, n-hexane, and heptanes were observed at 25 and 50 °C. No dibranched products were observed. Uncatalyzed reaction was undetectable.

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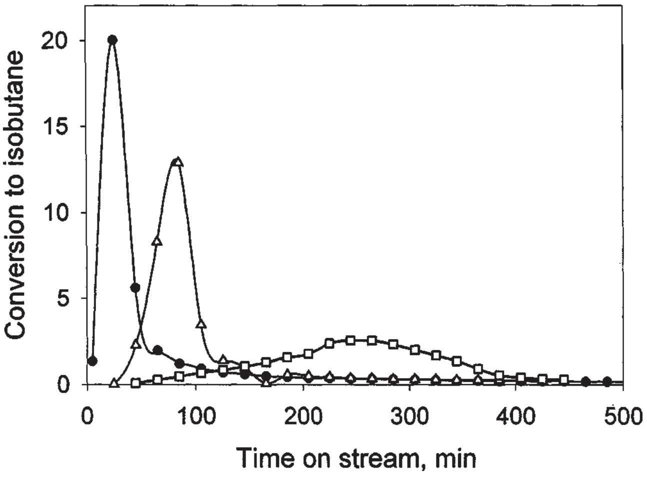


Figure 1. Effect of temperature on conversion of n-pentane into isobutane catalyzed by FMSZ in a flow reactor. Catalyst mass, 0.50 g; n-pentane partial pressure, 0.010 atm; feed flow rate, 20 ml (NTP)/min; (●) at 50 °C; (△) at 25 °C; (□) at 0 °C.

3.2. Catalyst break-in and deactivation

Conversion of n-pentane was characterized by a period of increasing conversion (the induction period) followed by declining conversion (catalyst deactivation). The length of the induction period was different for each product at a given temperature. The typical product was characterized by single maximum in the conversion versus on-stream time plot [15], but isopentane was characterized by two maxima – barely evident in the figure published earlier [15] and much more clearly discernible at the lowest temperature, $-25\,^{\circ}$C. The length of the induction period for each product decreased with increasing temperature, as illustrated in figure 1 for isobutane. The length of the induction period was almost independent of the reactant partial pressure and space velocity.

3.3. Estimation of reaction rates

The conversion at the end of the induction period defined by the maximum in conversion to a product was used as a measure of the fresh catalyst performance. Plots of such conversions versus inverse space velocity fall near straight lines through the origin, demonstrating nearly differential conversions; the slopes of the lines are measures of the initial rates of formation of the respective products for the fresh catalyst (table 1). As the conversion versus on-stream time curves characterizing isopentane include two maxima, the basis for estimating the rate was arbitrary – taken to be the greater of the two maxima. Data are not included in table 1 for reaction at $-25\,^{\circ}$C because the runs were not carried out long enough to complete the induction periods for each product. Some rates determined at 50 °C are relatively inaccurate because the induction times were too short to allow good estimates of the maximum conversions from plots of conversion versus on-stream time.

Table 1
Rates of formation of products from n-pentane catalyzed by Fe- and Mn-promoted sulfated zirconia.[a]

Temperature (°C)	Product	$10^9 \times$ rate[b]			
		FMSZ catalyst	PtFMSZ catalyst	PtFMSZ catalyst with H_2 in feed	SZ catalyst
0	isopentane	6.3	10.0	20.4	–
25	isopentane	23.4	44.4	31.3	–
50	isopentane	12.5[c]	16.4[c]	–	0.2
0	isobutane	15.5	15.6	11.7	–
25	isobutane	51.1	74.4	28.3	–
50	isobutane	57.1[c]	81.2[c]	–	0.2
0	3-MP	0.4	0.6	0.8	–
25	3-MP	1.0	2.0	1.0	–
50	3-MP	1.1[c]	1.4[c]	–	ND
0	2-MP	0.4	0.5	0.6	–
25	2-MP	1.2	2.0	1.0	–
50	2-MP	1.1[c]	1.6[c]	–	ND

[a] See text for statement of how rates were determined. Catalyst mass, 0.25 g; weight hourly space velocity, 0.078 g of n-pentane/(g of catalyst × h). When H_2 was present in the feed, the H_2 partial pressure was 0.20 atm.

[b] Units of rate: mol/(g of catalyst × s).

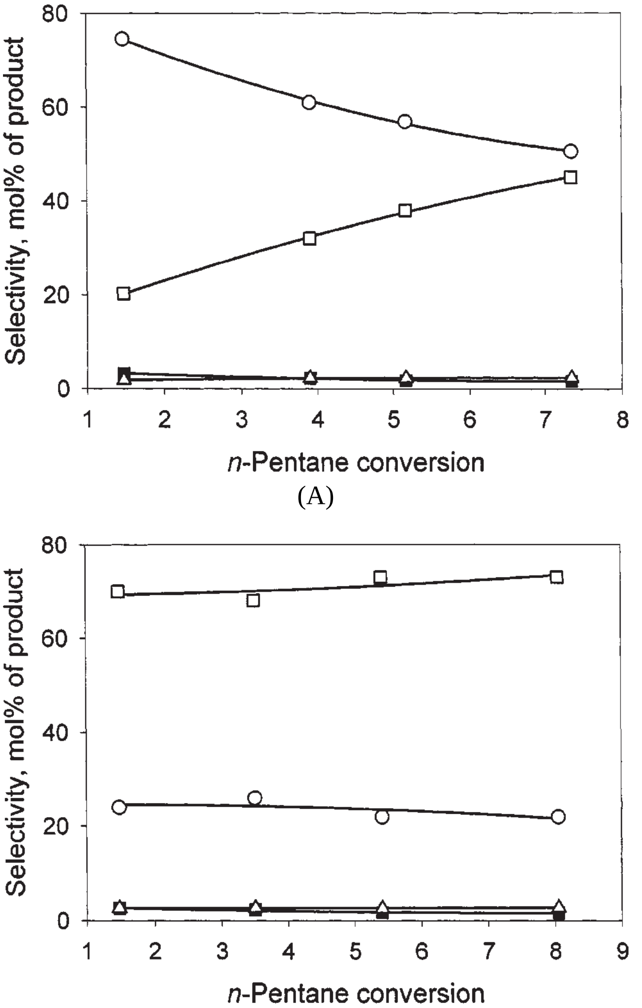
[c] Significant catalyst deactivation took place prior to measurement of conversion.

3.4. Product distributions

The data show that the product distribution in n-pentane conversion depends on the temperature as well as the time on stream [15]. Isopentane was a major product at the lowest temperature, but isobutane became predominant at higher temperatures. During the induction period, there was a decline in selectivity for isopentane formation that was nearly compensated by the increase in selectivity for isobutane formation [15]. The data indicate a period following the induction period of nearly constant product distribution as a function of time on stream.

Because the product distribution changed with time on stream, any plot of product distribution versus conversion is somewhat arbitrary. For reaction at 0 °C, figure 2(A) represents the performance of FMSZ during the induction period, when the n-pentane conversion was 73% of the maximum observed at the end of the induction period; this conversion was chosen because it occurred prior to the maximum in conversion to any one product. For comparison, figure 2(B) represents performance of this catalyst following the induction period, when the n-pentane conversion was again 73% of the maximum; this conversion occurred after the maximum in conversion to any one product.

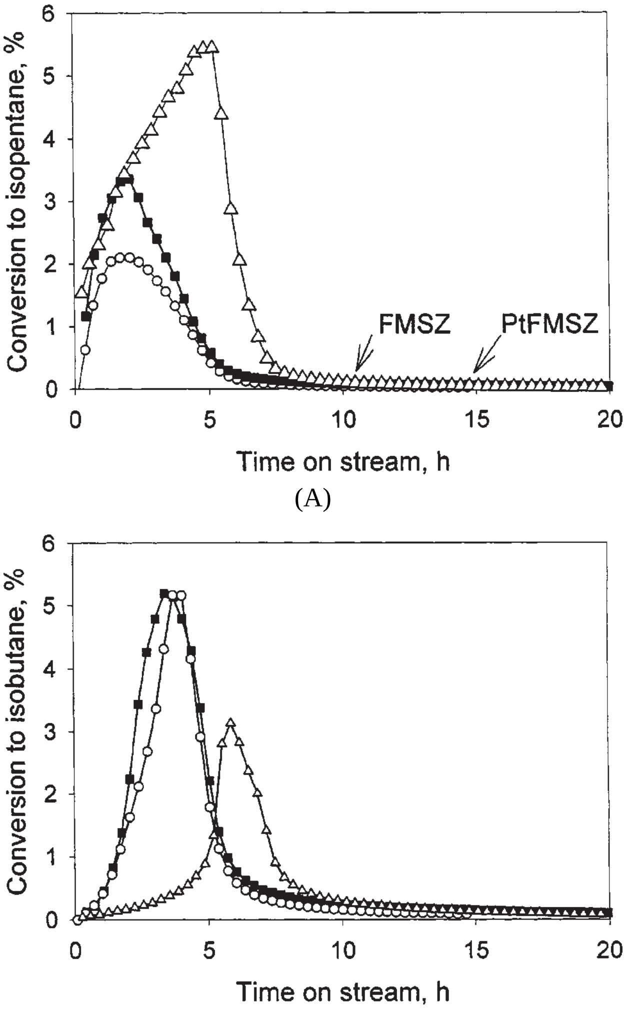
The comparison of figure 2 (A) and (B) shows a marked difference in the product distributions as a function of conversion before and after the time corresponding to the maximum conversion. Qualitatively, the same conclusion is supported by data plotted for different times on stream during and following the induction period and for different temperatures. The product distribution versus conversion plots (figure 2 (A) and (B)) show that the selectivities extrapolated to zero conversion are non-zero. The results



(A)

(B)

Figure 2. Product distributions observed for conversion of n-pentane during (A) and following (B) the induction period at 0 °C. The data were determined when the conversion was 73% of that determined at the maximum (the end of the induction period). Reaction conditions were as stated in the caption of figure 1, except for the catalyst mass, which was varied. (○) Isopentane; (□) isobutane; (■) 2-methylpentane; (△) 3-methylpentane.



(A)

(B)

Figure 3. Effect of addition of Pt to the catalyst and H_2 to the feed on the conversion of n-pentane into isopentane (A) and isobutane (B). Catalyst mass, 0.25 g; weight hourly space velocity, 0.078 g; n-pentane/(g of catalyst × h); when H_2 was in the feed, the H_2 partial pressure was 0.20 atm. (○) FMSZ; (■) PtFMSZ; (△) PtFMSZ with H_2 in feed. Arrows indicate time at which the total conversion declined to 3% of maximum.

of figure 2(B) show that the product distribution changed only little as a function of conversion following the induction period. The predominant product formed during the induction period, especially at the lowest conversions, was isopentane. The predominant product formed following the induction period was isobutane.

3.5. Effects of promoters

A satisfactory comparison of the performances of the unpromoted and promoted catalysts could be made only for reaction at 50 °C because the activity of the unpromoted catalyst was too low to allow quantitative measurements at lower temperatures. The rate data (table 1) show that the FMSZ was two orders of magnitude more active than the unpromoted sulfated zirconia. Evidence of the effect of Pt as a promoter in addition to Fe and Mn is also shown by the data of figure 3 (A) and (B) (for reaction at 0 °C) and table 1. The added Pt led to no measurable change in the length of the induction period, but it did lead to a modest increase in the rate of formation of isopentane and to a smaller increase in the rate of formation of isobutane. Because the added Pt led to increased activity over the whole period of observation of the catalyst performance, another measure of its benefit is provided by integrated values of the conversion. The conversion was integrated from the beginning of each run to the time when the conversion had declined to 3% of the maximum conversion (marked with arrows in figure 3(A)) (figure 4).

The effect of 0.2 atm of H_2 in the feed stream at 0 °C is shown by the data of figure 3 (A) and (B), where results are included for a feed without H_2. The data show that H_2 led to (a) an increased induction period for both isopentane and isobutane formation; (b) a decrease in the activity for formation of isobutane; and (c) an increase in the activity for isopentane formation (table 1).

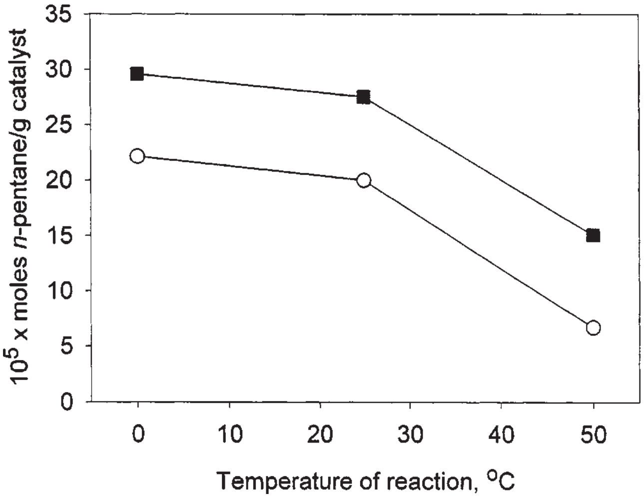


Figure 4. Effect of the addition of Pt to the FMSZ catalyst on the total number of moles of n-pentane converted before the conversion had declined to 3% of maximum. Catalyst mass, 0.25 g; weight hourly space velocity, 0.078 g of n-pentane/(g of catalyst × h). (○) FMSZ; (■) PtFMSZ.

4. Discussion

4.1. Reactions and reactivities

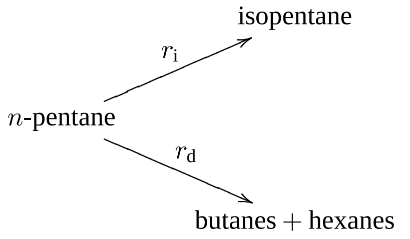
The occurrence of reaction even at temperatures as low as $-25\,^{\circ}\mathrm{C}$ shows that the promoted SZ is a highly active n-pentane isomerization catalyst, just as it is a highly active n-butane isomerization catalyst [4,5,10–14]. The pattern of an induction period followed by rapid deactivation is qualitatively the same as that observed for n-butane conversion in the presence of the FMSZ catalyst [5,6,10–12].

The reported results [4,6,12] indicate that n-butane isomerization catalyzed by FMSZ is accompanied by disproportionation, which, under some conditions, is nearly stoichiometric. A presumed analogy between the chemistries of n-butane and n-pentane conversions suggests the occurrence of n-pentane disproportionation, in agreement with the observation of butane and hexane products, but the ratios of these products do not correspond to stoichiometric disproportionation. We postulate that further disproportionation reactions occurred, converting the butane into propane and pentane and the hexanes into pentanes and heptanes, etc. Consistent with this expectation, propane, n-butane, hexanes, and heptanes were observed as (minor) products.

4.2. Reaction network

The product distribution data provide a basis for a postulated reaction network for n-pentane conversion catalyzed by FMSZ. The product distribution versus conversion plots (figure 2 (A) and (B)) lead to the identification of isobutane, isopentane, 2-MP, and 3-MP as primary products of n-pentane conversion, as the selectivity for formation of each was >0 in the limit of zero conversion. Consequently, we identify isomerization (giving isopentane) as a primary reaction. The other primary reaction products were evidently formed in a separate parallel reaction, disproportionation.

Thus, the simplified reaction network is represented as follows:



Consistent with the observation of propane and heptanes as minor products, we postulate that these were formed from butanes and hexanes, respectively, in secondary disproportionation reactions (not shown in the simplified network). However, even with this modification, the network still does not account for the observation that the minor products were formed in nonstoichiometric ratios.

If we approximate the rate of disproportionation r_d as the rate of isobutane formation from n-pentane, then the data of table 1 (representing the maximum rates of each reaction during the operation of the catalyst) show that the selectivity defined as the ratio of the rate of isomerization r_i to the rate of disproportionation r_d is about 0.41 at 0 °C, about 0.46 at 25 °C, and about 0.22 at 50 °C. We emphasize that the selectivities were dependent on on-stream time, and the values quoted in this paragraph represent only the values corresponding to the maxima in the conversion versus on-stream time plots.

4.3. Reaction mechanism

The product distributions are similar to those observed for n-pentane conversion in the presence of $HCl/AlCl_3$ [17]. Pines [18] interpreted these data in terms of isomerization and disproportionation reactions, also invoking the disproportionation of the product hexanes to give isobutane, which became the major product at high conversions. Thus, our proposed reaction network agrees with that of Pines for the reactions catalyzed by $HCl/AlCl_3$; the latter reactions are generally accepted to proceed via carbenium ion mechanisms.

Butane isomerization catalyzed by FMSZ has been suggested to take place by a bimolecular mechanism, involving the reaction of butyl cations with butenes [5,11,12]. The induction times characteristic of n-butane isomerization catalyzed by FMSZ were generally found to be the same as those characteristic of n-butane disproportionation [7]. As it is likely that the disproportionation reaction is bimolecular, the near equality of the induction times for disproportionation and isomerization was interpreted as evidence that the n-butane isomerization reaction is bimolecular [7].

In contrast, the induction times reported here for n-pentane disproportionation were consistently different from those observed for n-pentane isomerization. Assuming that the n-pentane disproportionation was bimolecular, we infer from the comparison that the n-pentane isomerization was not always bimolecular. The plausible alternative is that the n-pentane isomerization was monomolecular, as was already inferred for the reaction catalyzed by FMSZ [15] and SZ [19]. Because double maxima were observed for the formation of isopentane as a function of time on stream, we infer that both bimolecular and monomolecular n-pentane isomerization mechanisms were operative.

Considerations of carbenium ion stability [20] show that branching rearrangements of carbenium ions proceed via (substituted) protonated cyclopropane species, and the corresponding C_5 cation rearranges (consistent with a monomolecular mechanism of n-pentane isomerization) without the formation of a high-energy primary carbenium ion. In contrast, the corresponding C_4 cation can undergo a monomolecular rearrangement only via a primary carbenium ion. This latter mechanism is so unfavorable for n-butane isomerization that it is virtually excluded; rather, the bimolecular mechanism described above prevails, being energetically more favorable as it proceeds via nonprimary carbenium ions. The inference that n-pentane isomerization takes place both by a bimolecular mechanism and a monomolecular mechanism (with each involving secondary carbenium ions) is in accord with the observation that the rates of n-butane isomerization and n-pentane isomerization are approximately equal to each other, as both are inferred to proceed via secondary carbenium ions. The monomolecular mechanism is competitive with the bimolecular mechanism when the reactant is n-pentane because secondary carbenium ions form readily; in contrast, the monomolecular mechanism is virtually excluded for n-butane conversion because the secondary carbenium ion cannot form readily.

Because the selectivity for isomerization versus disproportionation changed strongly during the induction period, with isomerization dominating at the shortest times on stream, we suggest that the monomolecular isomerization mechanism predominated initially and that the bimolecular mechanism became dominant later, with the selectivities becoming almost independent of time on stream after the induction period. Thus, we infer that the nature of the surface species on the catalyst changed during the induction period in such a way as to disfavor the monomolecular mechanism and to favor the bimolecular mechanism. An inference is that the catalyst initially favored reactions that did not involve alkene intermediates. The alkenes and species that could have been equilibrated with them, such as carbenium ions, might have built up on the catalyst surface during the induction period. Perhaps the mechanism that was predominant initially (an initiation step), before much alkene was present, involved protonation of the n-pentane reactant by the catalyst, as has been suggested to occur for the less reactive alkanes ethane [21] and propane [22].

4.4. Influence of Fe and Mn promoters

The Fe and Mn promoters were reported to increase the activity of sulfated zirconia by two or three orders of magnitude for n-butane isomerization [4]. Similarly, the data reported here show that at 50 °C, these promoters increase the activity of SZ for n-pentane conversion by two orders of magnitude (table 1).

The roles of the Fe and Mn promoters are not yet fully explained. The alkane reactions may not be entirely acid-catalyzed. Although no direct evidence of enhancement in dehydrogenation activity by added Fe and Mn in sulfated zirconia has been observed in the product distribution data characterizing propane [22] and ethane [21] conversions, bifunctional catalysis has been suggested to explain the high activity of FMSZ for n-butane isomerization, whereby the promoters may be involved as initiators [23] or catalysts [11,24] in converting alkanes to alkenes by dehydrogenation; the alkenes are protonated by the acidic function of the catalyst to give carbenium ions. Alternatively, the catalyst might be a strong enough acid to protonate alkanes directly, giving carbonium ions (presumably transition states) that collapse to give carbenium ions [25]. The data presented here do not provide a basis for clarifying the role(s) of the Fe and Mn promoters.

4.5. Influence of Pt promoter

The effect of the Pt is to increase the activity of the Fe- and Mn-promoted catalyst slightly (figure 3 (A) and (B), table 1). The observation is qualitatively consistent with observations of the performance of Pt-promoted SZ [26]. The Pt hardly changed the product distribution or the time to maximum conversion; these results suggest that the Pt barely affected the reaction mechanism.

4.6. Influence of H_2 in the feed

The effect of H_2 in the feed on the performance of the Pt-promoted catalyst is shown for reaction at 0 °C in figure 3 (A) and (B). H_2 increased the activity of the catalyst for formation of isopentane but not for the formation of isobutane. This result suggests that the H_2 in the presence of Pt favored a pathway for monomolecular isomerization; a plausible suggestion is that H_2 served to keep the Pt surface clean, thus favoring dehydrogenation to give pentene, which would have been readily protonated to give carbenium ions that would undergo monomolecular isomerization. Thus, the role of H_2 and Pt may be comparable to that in classical catalytic reforming of naphtha. The implication of this suggestion is that the role of the Pt in the absence of H_2 was somehow suppressed, we suggest by the formation of carbonaceous deposits formed from alkene intermediates and associated with the bimolecular reactions.

We emphasize that the effects of temperature on the roles of Pt and H_2 are complex (table 1).

4.7. Potential for application of the promoted catalyst

The catalyst is highly active even at low temperatures, which is advantageous. However, it is not active for formation of dibranched products at the low conversions investigated in this work, which implies that it may not meet the most demanding criteria for production of high-octane-number alkanes. As the catalyst deactivates rapidly, we infer some modification to minimize the rate of deactivation; the effects of H_2 in the feed and Pt in the catalyst suggest that they would improve the chances of its application.

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