Manganese, iron, cobalt, nickel, and zinc as promoters of sulfated zirconia for *n*-butane isomerization

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First-row transition metals were tested in a flow reactor as promoters of sulfated zirconia for the isomerization of *n*-butane at 373 K and 0.005 bar *n*-butane partial pressure. The activity of each of the sulfated zirconia samples increased through a maximum and then decreased with time on stream. In order of increasing activity measured at the maximum, the effect of the promoters increased from right to left in the periodic table: zinc, nickel, cobalt, iron, and manganese. Iron and manganese increased the activity by 2–3 orders of magnitude. The causes of the promoter action are not elucidated; the promoters may play noncatalytic roles as initiators.

Keywords: sulfated zirconia; manganese; iron; cobalt; nickel; zinc; *n*-butane isomerization

1. Introduction

Sulfated zirconia based materials have attracted interest as solid acids for low-temperature alkane isomerization. Iron- and manganese-promoted sulfated zirconia allows the conversion of *n*-butane even at room temperature [1–6]. The activity is 2–3 orders of magnitude greater than that of sulfated zirconia [1]. However, after a period of increasing conversion, the activity rapidly declines [2].

Metals other than iron and manganese are also promoters of sulfated zirconia [7–9], with the iron–manganese combination being the best yet reported among the first-row transition metals. Jatia et al. [5] found iron to be an order-of-magnitude better promoter than manganese, whereas Resasco et al. [10] found that manganese alone was not a promoter, although iron was. The combination was found by each group to be better than iron alone. Resasco et al. [10] suggested that manganese affects the dispersion of the iron species. Adeeva et al. [4] hypothesized that the isomerization of butane proceeds through a bimolecular mechanism involving C_8 intermediates formed from butenes and C_4 carbenium ions; the promoting effect of the transition metal oxides could thus involve their activity as butane dehydrogenation catalysts. The formation of C_8 intermediates was confirmed by results of ^{13}C tracer experiments showing a binomial ^{13}C distribution in the product. Wan et al. [6] suggested that butenes result from dehydrogenation of butane by redox active iron oxy sites.

There is little literature on the characterization of iron- and manganese-promoted sulfated zirconia [11,12]. According to Coelho et al. [13], nickel showed a promoting effect comparable to that of iron and manganese; others have also observed promotion by nickel [14].

As the roles of the first-row transition metal promoters for *n*-butane isomerization are not well documented, our goals were to compare manganese, iron, cobalt, nickel, and zinc as promoters of sulfated zirconia for *n*-butane isomerization and to compare the promotion by iron and manganese separately with the promotion by the combination of the two.

2. Experimental

2.1. Sample preparation and surface area measurement

The materials used in the sample preparations were the following: sulfated zirconium hydroxide (3.4 wt% SO_3, Magnesium Elektron, Inc., XZO-682/01); iron(III) nitrate nonahydrate (Aldrich, 98%); manganese(II) nitrate (Aldrich, 98%); cobalt(II) nitrate hexahydrate (Aldrich, 99.999%); nickel(II) nitrate hexahydrate (Strem, 99.9985%); and zinc(II) nitrate hexahydrate (Sigma, 98%).

The composition of each sample was chosen to provide a basis for comparison with that of the previously reported iron- and manganese-promoted sulfated zirconia [1,2,15]; containing approximately 1.5 wt% iron and 0.5 wt% manganese, corresponding to a total metal content of 360 (μmol of promoter metal)/(g of sample). All samples thus contained the same number of promoter atoms per unit mass, which corresponds to approximately 2 wt% of the promoter metal in each.

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The sulfated zirconium hydroxide was dried for at least 24 h at 388 K. The samples were prepared from it by incipient wetness impregnation [2]. Each sample was calcined for 3 h at 923 K in a muffle furnace with the temperature ramped at a rate of 3 K/min.

BET surface areas of the samples were measured with an Advanced Scientific Designs RXM-100 adsorption/reaction/characterization system after pretreatment at 373 K for 1 h in vacuum.

2.2. Catalytic testing

Each sample was tested in a once-through quartz flow reactor at atmospheric pressure with on-line product analysis by gas chromatography and flame ionization detection [2]. The powders were pretreated in N_2 flowing at 35 ml(NTP)/min. The temperature was ramped from room temperature to 723 K within 1 h and held at 723 K for 1.5 h. Each sample was cooled to reaction temperature in flowing N_2. The feed to the reactor was a mixture of 1 mol% *n*-butane in N_2 (Liquid Carbonic, < 5 ppm isobutane) and N_2 (Liquid Carbonic, 99.999%). The following reaction conditions were used: temperature, 373 K; feed *n*-butane partial pressure, 0.005 bar (with the balance being N_2); pressure, 1 bar; sample mass, 1.0 g; total feed flow rate, 80 ml(NTP)/min. Iron-promoted and manganese-promoted sulfated zirconia were also tested at 323 K and 0.01 bar *n*-butane partial pressure.

3. Results

A list of the samples and their BET surface areas is given in table 1 with the colors before and after calcination.

Terms used to represent the sample performance include the following: Normalized conversion to a gas-phase product is defined as (concentration of individual gas-phase product × number of carbon atoms in individual product)/(4 × *n*-butane concentration in feed). The conversion to gas-phase products is taken to be the sum of the conversions to the individual products. Selectivity to a product is defined as (100 × number of moles of the gas-phase product)/(number of moles of all the gas-phase products).

The reproducibility of the conversions was typically ±15% for a particular sample. The performance was sensitive to the preparation conditions in ways that are not yet resolved, and the activity of a sample sometimes differed as much as twofold from one preparation to the next. The performance of some samples changed so rapidly during the first few minutes on stream that only imprecise data could be obtained to characterize the initial performance. Nonetheless, the differences in performance from one promoted sulfated zirconia to another are large enough to distinguish them clearly.

The conversion observed in the presence of unpromoted sulfated zirconia was low relative to that observed for the promoted samples (fig. 1), and isobutane was the only gas-phase product observed at the low conversions investigated in these experiments. The presence of nickel in the sample led to only a modest increase in activity (fig. 1), and again only isobutane was observed in the product stream; the maximum conversion was observed between 1 and 2.5 h on stream. Like nickel, zinc led to a modest increase in the activity (fig. 1), with the gas-phase product being isobutane and the changes with time on stream being small.

The performance of cobalt-promoted sulfated zirconia was characterized by an initial steady increase in activity (fig. 2), with the conversion reaching 1% after an induction period of about 20 h and then declining. Propane and pentanes were sometimes observed as side products, but the selectivity for isobutane was always $> 95\%$.

Manganese-promoted sulfated zirconia was characterized by a high initial activity, with conversions up to 15–20% at about 5 min on stream (fig. 3). Besides isobutane, the predominant product (formed with a selectivity $> 80\%$ after 5 min on stream and $> 95\%$ after 30 min on stream), propane and pentanes were also observed, along with traces of methane after 5 min on stream. Within 30 min, the activity declined to conversions $< 2\%$. Propane and pentanes were observed for about 1 h, and at longer times on stream the selectivity for iso-

Table 1
Colors of the samples and BET surface areas after calcination

Sample	Color		BET surface area (m^2/g)
	prior to calcination	after calcination	
sulfated zirconia (SZ)	white	white	100[a]
manganese-promoted (MnSZ)	light pink	blue-gray	70
iron-promoted (FeSZ)	ochre	ochre/rust	80
cobalt-promoted (CoSZ)	pink/purple	pale purple	60
nickel-promoted (NiSZ)	light green	pale purple/gray	65
zinc-promoted (ZnSZ)	white	white	50

[a] Data from Magnesium Elektron, Inc.

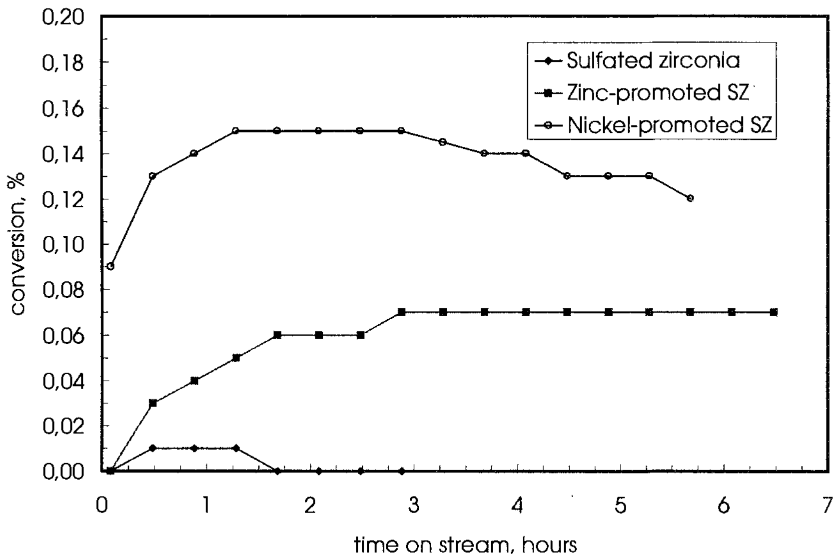

Fig. 1. *n*-butane conversion in a flow reactor in the presence of sulfated zirconia (SZ) (sample mass, 1.5 g); zinc-promoted sulfated zirconia (1 g); and nickel-promoted sulfated zirconia (1 g). Temperature, 373 K; *n*-butane partial pressure, 0.005 bar; total feed flow rate, 80 ml (NTP)/min.

butane was 100%. At 323 K when the reaction was conducted at a 0.01 bar *n*-butane partial pressure, an induction period of about 1 h was observed, with a maximum conversion between 5 and 10% (fig. 4). The relative decrease in activity after the maximum conversion was far less than that observed at 373 K. Propane and pentanes were observed in the product stream for several hours, but the selectivity to isobutane was always > 95%.

The performance of the iron-promoted sulfated zirconia at 373 K was characterized by an induction period with a steeply increasing rate (fig. 3). The conversion reached its maximum of about 10% within the first hour on stream. After the initial sharp decrease in activity, a slow decline in activity was observed. The products were isobutane (selectivity > 85%), propane, and pentanes. The performance at 323 K (fig. 4) was similar to that at 373 K.

4. Discussion

The data show that zinc and nickel have only modest effects as promoters; cobalt has a significant effect, giving more than an order of magnitude increase in activity; and iron and manganese increase the activity by two or three orders of magnitude. Even the largely deactivated iron- and manganese-promoted sulfated zirconia is

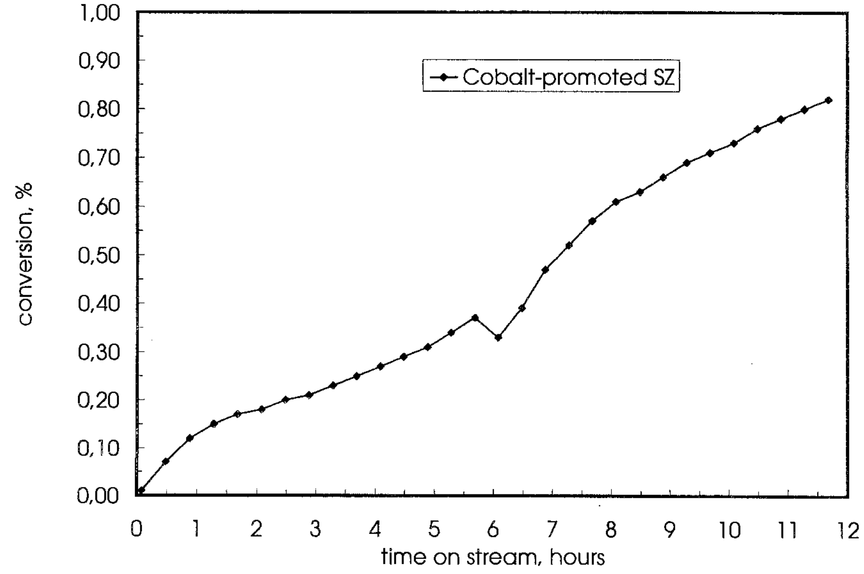

Fig. 2. *n*-butane conversion in a flow reactor in the presence of cobalt-promoted sulfated zirconia (sample mass, 1 g). Temperature, 373 K; *n*-butane partial pressure, 0.005 bar; total feed flow rate, 80 ml (NTP)/min.

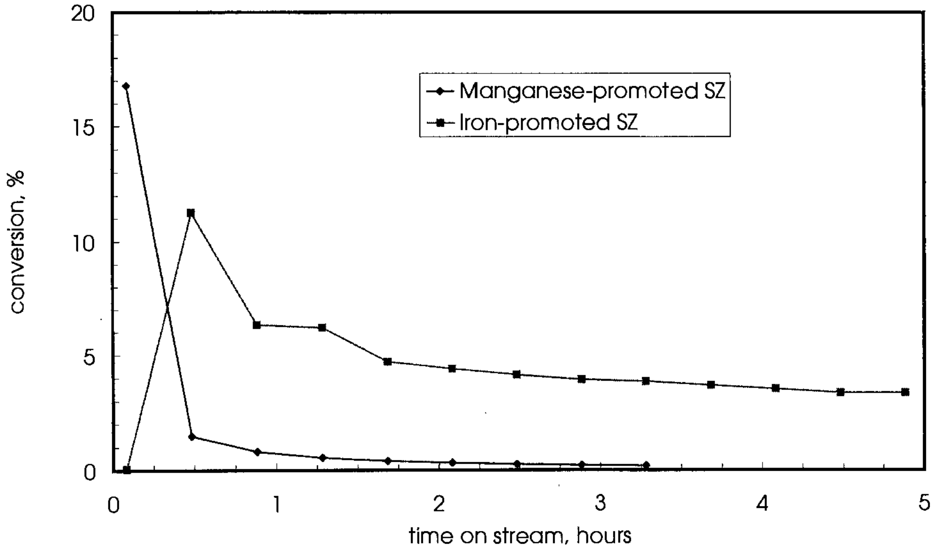

Fig. 3. *n*-butane conversion in a flow reactor in the presence of iron-promoted sulfated zirconia (sample mass, 1 g) and manganese-promoted sulfated zirconia (1 g). Temperature, 373 K; *n*-butane partial pressure, 0.005 bar; total feed flow rate, 80 ml (NTP)/min.

much more active than the other promoted sulfated zirconias at their maximum activities. Notwithstanding the large differences in activity, the selectivities for the formation of the detectable products were similar for all investigated samples.

The activities of the promoted sulfated zirconias do not correlate with the BET surface areas, and thus we infer that there are distinct chemical effects of the different promoters. However, the data are not sufficient to determine whether the promoters are differently dispersed in the various promoted sulfated zirconias.

Although the activities differ significantly from one promoted sulfated zirconia to another, the reaction profiles were all found to be characterized by an induction period of increasing conversion followed by a declining conversion. The more active the sample, the shorter was each stage of operation; the induction period characteristic of the manganese-promoted sulfated zirconia was observed only at 323 K (fig. 4) and was presumably too short to observe at 373 K.

Thus our data do not agree with the result of Coelho et al. [13] and Resasco et al. [10] that manganese alone without iron is not a promoter; their reactions were conducted at 373 K and at much higher *n*-butane partial pressures than ours, i.e., 0.25 bar. Since the manganese-promoted sulfated zirconia is rapidly deactivated even at 0.005 bar *n*-butane partial pressure, we suggest that the conversion might have rapidly dropped to so low a value as to become immeasurable under Coelho's conditions.

Nickel was found to enhance the catalytic activity

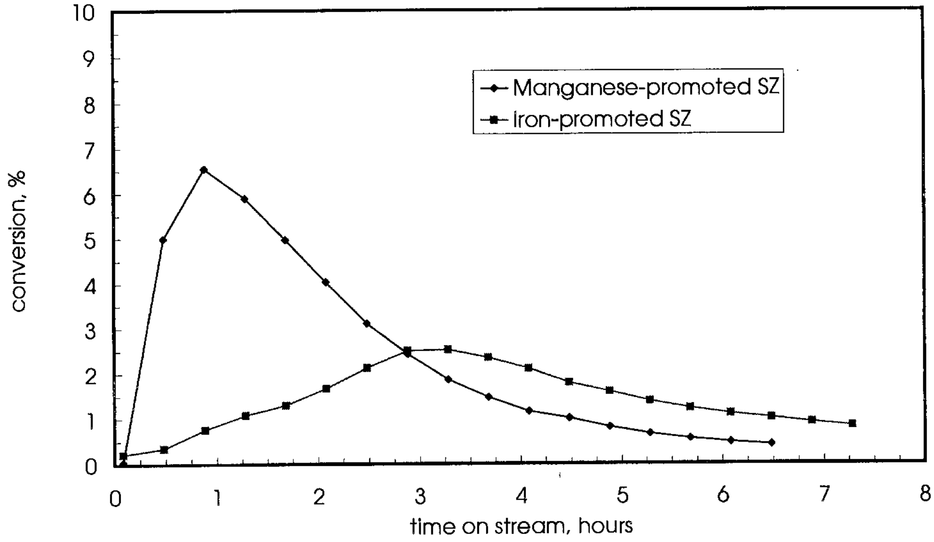

Fig. 4. *n*-butane conversion in a flow reactor in the presence of iron-promoted sulfated zirconia (sample mass, 1 g) and manganese-promoted sulfated zirconia (1 g). Temperature, 323 K; *n*-butane partial pressure, 0.01 bar; total feed flow rate, 80 ml (NTP)/min.

Table 2
Number of molecules n-butane converted per number of promoter atoms present in the sample integrated over time on stream

Sample	Temperature (K)	Time on stream (h)	Mol of n-butane converted to gas-phase products per mol of promoter metal
MnSZ	323	6.5	0.96
FeSZ	323	7.5	0.64
MnSZ	373	3.5	0.15
FeSZ	373	5.0	0.67

for n-butane conversion only modestly, which also seemingly contradicts the results of Coelho et al. [13]. Their samples contained 8 wt% sulfur and up to 1% nickel, and their test conditions were different from ours, as they applied a much higher n-butane partial pressure, the mole fraction of n-butane in the feed being 0.25. The promotion effect of nickel observed by Coelho et al. [13] was roughly the same as what they observed for the iron-manganese combination (although they did not regard their data as a basis for quantitative comparisons of promoters). The difference between their results and ours suggests a strong dependence of promoter effects on reaction and/or sample preparation conditions; we reemphasize the importance of accounting for deactivation in comparisons of promoters. Thus although our results confirm that iron and manganese are the best promoters with regard to maximum activity known for sulfated zirconia, the conclusion should be restricted to catalysts containing about 2 wt% promoter and 4 wt% sulfate operated under conditions of our experiments.

The conversion profiles were used to estimate roughly the number of turnovers per promoter atom in each promoted catalyst by integration to determine the number of moles of n-butane that were converted to gas-phase products over the time on stream, assuming that each promoter atom might be a potential site (table 2). This calculation does not account for promoter atoms that are inaccessible because of poor dispersion.

The number of turnovers per manganese promoter atom was about unity at 373 K, and the catalytic activity had declined to almost zero by the end of the experiment (fig. 3). The comparable values shown for the other catalysts in table 2 are less than unity (although the catalysts still had measurable activities when the experiments were terminated).

Thus the data raise the question of whether first-row transition metal promoters may be playing noncatalytic roles. These metals might be initiators rather than catalysts, consistent with the proposal [4] that butane is dehydrogenated in association with the metal to give butene.

5. Conclusions

The first-row transition metals manganese, iron, cobalt, nickel, and zinc are all promoters of sulfated zirconia for the isomerization of n-butane in a flow reactor at 373 K and 0.005 bar n-butane partial pressure. Promoter contents of approximately 2 wt%, introduced by incipient wetness impregnation lead to increased reaction rates but barely affect the selectivity. Zinc and nickel have only modest effects as promoters; cobalt has a significant effect, giving more than an order of magnitude increase in activity; and iron and manganese increase the activity by two or three orders of magnitude. The promoter effects are short lived. The causes of the promoter action are not elucidated; the promoters may play noncatalytic roles as initiators.

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