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Superacid Catalysis of Light Hydrocarbon Conversion

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Report written by

Bruce C. Gates
Department of Chemical Engineering and Materials Science
University of California
Davis, CA 95616
telephone: (916) 752-3953
FAX: (916) 752-1031
Email: BCGATES@Poppy.engr.ucdavis.edu

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SUMMARY

Transition metal promoters of sulfated zirconia increase its catalytic activity for the conversion of \(n\)-butane. The promoter effects vary from one transition metal to another in the family zinc, iron, nickel, cobalt, and manganese. The most active catalyst so far tested is promoted by both iron and manganese. This catalyst is two or more orders of magnitude more active than unpromoted sulfated zirconia. The manganese promoter alone markedly increases the catalytic activity, but the activity declines very rapidly with time on stream in the flow reactor. Under the same experimental conditions, iron has a smaller but longer-lasting effect as a promoter than manganese, and to a first approximation, the iron- and manganese-promoted catalyst shows a behavior that is a superposition of those of the two individual promoters.

INTRODUCTION

Iron- and manganese-promoted sulfated zirconia has drawn attention because it catalyzes \(n\)-butane isomerization even at temperatures as low as room temperature.\(^1\)-\(^6\) The activity of the promoted catalyst is about two orders of magnitude greater than that of sulfated zirconia,\(^2\) but the catalyst deactivates rapidly, following an induction period of increasing activity.

Iron-promoted, manganese-promoted, and iron- and manganese-promoted sulfated zirconia were investigated by Coelho et al.,\(^7\) who used X-ray photoelectron spectroscopy in combination with catalytic reaction experiments. On the basis of catalyst performance data and the observation that manganese itself does not act as a promoter, they suggested that manganese increases the dispersion of the iron surface species, which are the promoters. Wan et al.\(^8\) suggested that iron plays the role of a redox initiator, reacting with \(n\)-butane to form butenes, which are then protonated and undergo carbocation reactions to give the isomerization product.

Group 8 metals have also been investigated as promoters, including platinum,\(^9\) iridium, osmium, palladium, osmium, ruthenium and rhodium.\(^10\) Among these, iridium and platinum were found to give the most active catalysts for \(n\)-butane isomerization. Platinum has been investigated extensively because of its capability to stabilize sulfated zirconia in catalytic operation in the presence of \(\text{H}_2\). Only little work has
been published with regard to other first-row transition metals; nickel showed a promoting effect comparable to that of iron and manganese.\textsuperscript{7}

As the roles of the promoters are not yet well resolved, our goals were to investigate a family of first-row transition metals (cobalt, nickel, and zinc) as promoters of sulfated zirconia for \textit{n}-butane isomerization and to compare the performance of these materials with that of iron-, manganese-, and iron- and manganese-promoted sulfated zirconia.

**EXPERIMENTAL**

**Materials**

The materials were the following: Zirconium hydroxide, 3.4 wt\% SO\textsubscript{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%); zinc(II) nitrate hexahydrate (Sigma, 98%); \textit{n}-butane (Liquid Carbonic, 2 ppm isobutane), N\textsubscript{2} (Liquid Carbonic 99.999%).

**Catalyst preparation**

The composition of each catalyst was chosen to provide a basis for comparison with that of the iron- and manganese-promoted sulfated zirconia (prepared in a slightly different fashion), which contained 1.5 wt\% iron and 0.5 wt\% manganese, corresponding to a total metal content of 360 mol of promoter metal/g of catalyst. All catalysts thus contained this same number of promoter atoms per unit mass.

The support (zirconium hydroxide) was dried for at least 24 h at 388 K. The catalysts were prepared by incipient wetness impregnation. Each catalyst was calcined for 3 h at 923 K in a muffle furnace with the temperature ramped at 3K/min.

**Catalyst testing**

Each sample was tested in a once-through quartz flow reactor with on-line product analysis by gas chromatography (GC). The catalyst powders were pretreated in N\textsubscript{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. The system was cooled down to reaction temperature in flowing N\textsubscript{2}. The following standard reaction conditions were used: temperature, 373 K; pressure, 1 bar; feed \textit{n}-butane partial pressure, 0.005 bar (with
the balance being N₂); catalyst mass, 1.0 g; feed flow rate, 80 ml(NTP)/min. Additional experiments were conducted at 323 K with a n-butane partial pressure of 0.01 bar. In one set of experiments, the temperature was increased stepwise from 323 to 423 and then to 523 K.

RESULTS

Description of the samples

Sulfated zirconia is a white powder; the sulfated zirconia samples promoted with the following metals had the following colors: manganese, light pink prior to calcination and blue-gray thereafter; iron, ochre before and ochre/rust colored after calcination; cobalt: pink/purple before calcination and pale purple thereafter (turning purple/blurish during pretreatment prior to catalytic reaction); nickel, light green before calcination, pale purple/gray thereafter, and brownish after catalytic reaction; zinc, white at all stages.

Catalyst performance: Conversion, selectivity, and carbon balances

Normalized conversion to gas-phase products is defined as follows: sum of (concentration of individual gas-phase product \( \times \) number of carbon atoms in individual product) divided by (4 \( \times \) butane concentration in feed). Selectivity to a product is defined as 100 \( \times \) number of moles of the gas-phase product divided by the number of moles of all the gas-phase products.

The reproducibility of the conversions was typically \( \pm 15\% \) for a particular catalyst sample. The catalyst performance was sensitive to the preparation conditions in ways that are not resolved, and the activity of a particular catalyst sometimes differed twofold from one preparation to the next. However, the order of magnitude of the conversion was reproducible and allowed for an evaluation of the order of the promoting effect.

The performance of the catalysts is summarized in the following paragraphs. Unless otherwise mentioned, the data were obtained under the standard reactions conditions.

Sulfated zirconia (SZ)

The conversion observed in the presence of unpromoted sulfated zirconia was < 0.1%, and isobutane was the only product.

Nickel-promoted sulfated zirconia (NiSZ)
The presence of nickel in the catalyst did not lead to a significant promotion (Fig. 1). The conversion showed a slight increase followed by a slow decrease with time on stream, the maximum conversion being observed between 1 and 2.5 h on stream. The only detectable gas-phase product was isobutane.

*Cobalt-promoted sulfated zirconia (CoSZ)*

The performance of cobalt-promoted sulfated zirconia is characterized by a steady increase in activity (Fig. 1), reaching a conversion of 1% after approximately 20 h. In one experiment, the conversion did not decline significantly even after 34 h. Propane and pentanes were sometimes observed as side products, but the selectivity for isobutane was > 95%.

*Zinc-promoted sulfated zirconia (ZnSZ)*

The conversion of n-butane in the presence of zinc-promoted sulfated zirconia was about the same as that observed for the unpromoted sulfated zirconia, and the changes with time on stream were negligible. The only observed product was isobutane.

*Manganese-promoted sulfated zirconia (MnSZ)*

Manganese-promoted sulfated zirconia was characterized by a high initial activity, with conversions up to 15-20% at about 5 min on stream (Fig. 2). Only few samples of the flowing product were collected because of the time required for the GC analysis, and thus the data do not allow a good resolution of the reaction profile at short times on stream or an exact determination of the maximum conversion. Besides isobutane, which was 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 and ethane, which were detected in the product stream after 5 min on stream. Within 30 min, the activity declined sharply to conversions < 2%. Propane and pentanes were observed for about 1 h, and at longer times on stream the selectivity for isobutane was 100%.

At 323 K when the reaction was conducted at a 0.01 bar n-butane partial pressure, an induction period of about an hour was observed, with a maximum conversion between 5 and 10% (Fig. 3). 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%.

Iron-promoted sulfated zirconia (FeSZ)

The performance of the iron-promoted sulfated zirconia is characterized by an induction period with a steeply increasing rate (Fig. 2). The conversion reached its maximum of about 10% within the first hour on stream; however, the estimate of the maximum conversion is imprecise because of the rapid change. After a sharp decrease in activity, the reaction continued at a conversion of about 5%. A slow decrease with time on stream was observed. Besides isobutane, which formed with >85% selectivity, propane and pentanes formed.

At 323 K, the maximum in conversion was observed at a longer time on stream than at 373 K, and the conversion did not exceed a few percent. The predominant product was isobutane (> 90% selectivity), but a steady production of propane and pentanes started within the first hour.

DISCUSSION

The data demonstrate that all the transition metals tested are promoters for the butane isomerization reaction, but their effects are not all the same. The effect of zinc as a promoter is small. Nickel enhances the activity for n-butane conversion only a little, which seemingly contradicts the results of Coelho et al.7 Co shows the greatest long-term stability, but the activity is not high. Iron and manganese increase the activity by an order of magnitude more than the other promoters.

However, the performance of the iron is markedly different from that of manganese (although the comparison is not perfect because the conversions were different for the two samples, about 10% for the Fe-promoted sample and about 15-20% for the manganese-promoted sample). The manganese-promoted sulfated zirconia undergoes an extremely fast deactivation after a rapid induction period, which was only observed at 323 K. Coelho et al.7 stated that manganese alone without iron does not have a promoting effect; however, their reactions were conducted at 373 K at much higher n-butane partial pressures than ours, i.e., at 0.25 bar and higher. Since the manganese-promoted sulfated zirconia is rapidly deactivated even at 0.005 bar n-butane partial pressure, we suspect that the conversion might drop to immeasurably
low values within seconds or minutes at such high pressures, which could explain why the effect was not observed by Coelho et al.

All the promoted and unpromoted samples convert n-butane to the same products, predominantly isobutane, but the experiments at higher temperatures show that at 423-523 K all the samples, including sulfated zirconia itself, catalyze formation of propane and pentanes. Additional products (methane and ethane) were observed only for the manganese-promoted catalyst, which gave the highest conversions at the maximum at 373 K.

Similar profiles were observed for all the catalysts, as the n-butane conversion increased during an induction period and then declined. Qualitatively, these profiles are the same for all the catalyst, but quantitatively they are all different, with different lengths of the induction period and different catalytic activities, e.g., at the maximum at the end of the induction period. The differences arise because the catalysts have different activities and because the reaction conditions are not identical for all the experiments.

To a first approximation, the profile observed for the iron- and manganese-promoted catalyst appears to be superposition of the profiles for the iron- and the manganese-promoted catalysts. We suggest that the effects of the two promoters are additive. We emphasize that this is a preliminary conclusion only.

REFERENCES


FIGURE CAPTIONS

Fig. 1. Normalized conversion to gas-phase products in a flow reactor. Cobalt- (CoSZ), nickel- (NiSZ) and zinc- (ZnSZ) promoted sulfated zirconia. Mass of catalyst = 1 g; flow rate = 80 ml/min; temperature = 373 K; *n*-butane partial pressure = 0.005 bar, pressure atmospheric.

Fig. 2. Normalized conversion to gas-phase products in a flow reactor. Iron- (FeSZ) and manganese- (MnSZ) promoted sulfated zirconia. Mass of catalyst = 1 g; flow rate = 80 ml/min; temperature = 373 K; *n*-butane partial pressure = 0.005 bar, pressure atmospheric.
normalized conversion to gas phase products [%]

CoSZ

ZnSZ

NiSZ

Fig. 1

time on stream [min]
normalized conversion to gas phase products [%]