

Silver Supported on Zeolite as Catalyst for the Oxidation of Olefins

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The preparation of Ag-X and Ag,Ca-X zeolites, and their properties as catalysts for the oxidation of cyclohexene by air, were studied. The catalysts were prepared by ion-exchange of zeolite 13X, and subsequent reduction with hydrogen. The oxidation of cyclohexene was performed in a tubular reactor, at 270°C and atmospheric pressure and the conversion was 6-8%. The products obtained, identified by gas chromatography and infrared spectroscopy, were cyclohexene oxide, 2-cyclohexene-1-one, 1-cyclopentene-1-carboxaldehyde, and 1,6-hexanedial. Only traces of CO₂ (0.2%) were detected. The selectivity of the catalysts was affected by altering the calcium content; thus, Ag-X showed rather high selectivity for the epoxide, while in the presence of Ca the main product was 1-cyclopentene-1-carboxaldehyde.

INTRODUCTION

Silver is a powerful catalyst for the oxidation of ethylene into ethylene oxide, and selectivities up to 80% are obtained in industrial processes based on this reaction (1-3). However, the silver-containing catalysts that are active in the oxidation of ethylene generally fail to oxidize significantly higher olefins into the corresponding epoxides. In most cases, the predominant product of the oxidation is carbon dioxide (4-6). Nondestructive oxidation of higher olefins can be performed in the gas phase with catalysts containing the oxides of other metals, such as bismuth or molybdenum; however, the predominant products are not the epoxides but unsaturated aldehydes and other oxygenated compounds (7-9). The products seem to result from reactions that follow attack at the allylic position and not from reactions involving oxidation of the olefinic bond.

A plausible explanation for the difficulty to perform significant epoxidation of higher olefins than ethylene, in gas-phase catalytic reactions, is based on the lability of the C-H bond at the allylic position (6). Thus,

with a strong oxidation catalyst capable of attacking the olefinic bond, such as silver, the oxidation process which starts with the subtraction of hydrogen from an allylic position ends with total destruction of the organic molecule. With a weaker oxidation catalyst, such as bismuth, the dehydrogenation at the allylic carbon often leads to the formation of some valuable oxygenated compounds but the olefinic bond is not epoxidized.

A publication by Van Sickle and Prest (10) indicated that it should be possible to design a catalyst for the epoxidation of higher olefins by using a zeolite in combination with an appropriate metal. Aiming at studying the oxidation of olefins in the adsorbed state, these workers allowed olefins such as butenes and hexene to be adsorbed on samples of a cobalt-exchanged zeolite, and submitted them to oxidation. The products of the reaction remained in the adsorbed state and extraction methods had to be applied in order to separate them from the zeolite. However, the nature of these products indicated that attack on the olefinic bond had predominated over attack at the allylic position. Following these results, we prepared a catalyst for the epoxidation of higher olefins by introducing silver into a

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zeolitic material, and we tested it with cyclohexene in a flow reactor. We used a cyclic olefin since straight-chain olefins are expected to produce a complex mixture of products due to isomerization reactions accompanying oxidation (11, 12). In an attempt to gain more information on the nature of the reaction, we also prepared and investigated a series of catalysts containing various amounts of calcium, in addition to the silver.

EXPERIMENTAL

Preparation of the Catalysts

The zeolite used was molecular sieve 13X-Na form, $\frac{1}{8}$ -in. pellets (BDH, England). Silver was introduced by ion-exchanging the sodium ions originally present, and it was subsequently reduced to metallic silver. The procedure used was as follows. A 0.04 M solution of silver acetate was allowed to flow at 20 ml/min through a column containing the zeolite (100 ml bed), and elution was stopped when the concentration of Ag^+ in the outflowing stream reached 90% of the concentration of the inflowing solution. The exchanged zeolite was washed with deionized water, dried at 395 K, heated in a stream of nitrogen at 625 K during 4 h, and finally reduced by a stream of hydrogen at 635 K, during 4 h. The final product contained 2.78 mmol Ag per g catalyst.

Catalysts containing both silver and calcium were prepared from the fully exchanged Ag^+ -containing zeolite (see

above), by reequilibrating it with a calcium acetate solution (100 ml/g zeolite) of either 0.05, 0.1, or 0.5 M, in a batch procedure. The time course of this back-exchange process was followed by monitoring the concentration of Ag^+ released into the supernatant liquid. Using this procedure we could easily control the metal loading in the products. The doubly exchanged zeolites thus obtained were washed, dried, heated and reduced similarly to the singly exchanged ones. The silver and calcium contents of the catalysts prepared are given in Table 1.

Apparatus

Oxidation of cyclohexene was performed in a 2-cm-diameter tubular flow reactor made of glass. The bed of catalyst was 2-cm deep. The variation of the temperature during the reaction did not exceed 0.5 K. The reaction mixture was prepared by vaporizing a stream of liquid cyclohexene, delivered by a syringe pump, into a stream of air flowing at a known velocity. Vaporization took place in a packed vessel maintained at 395 K.

All the experiments reported in this paper were performed under the following conditions: temperature 545 K, atmospheric pressure, space velocity 0.7 μmol cyclohexene per ml catalyst per s. The molar ratio of cyclohexene to oxygen was 1:0.2, and this was obtained by mixing cyclohexene vapor and air at a 1:1 (v/v) ratio.

Analytical Procedures

Quantitative analyses of Ag^+ in aqueous solutions were performed by titration with NaCl (the Mohr procedure).

Infrared spectra of liquid samples were obtained with a Perkin-Elmer Model 1576 spectrophotometer, using cells equipped with NaCl windows.

Gas chromatographic analyses were performed with either a Packard Model 802 or a GowMac Model 69-552 chromatograph, both equipped with thermal conductivity detectors.

The composition of the reaction products

TABLE 1

Composition of the Catalysts

Composition	Catalyst designation			
	HL-20	HL-30	HL-40	HL-50
Ag, mmol/g catalyst	2.78	2.58	2.32	2.14
Ca, mmol/g catalyst ^a	0	0.15	0.28	0.43
Mole ratio Ca to Ca + Ag	0	0.053	0.105	0.16

^a Determined from the amount of Ag^+ liberated during the Ag^+ -to- Ca^{2+} ion exchange operation, and assuming that each Ca ion replaces two Ag ions.

was determined by gas chromatographic and ir spectrophotometric analyses. To this aim, the gaseous stream leaving the reactor was passed through an acetone/dry-ice-cooled trap, and the resulting liquid and gas phases were analyzed separately.

Samples of the liquid thus collected were chromatographed on a 180-cm column of Carbowax 20 M on Chromosorb W, maintained at 438 K. The carrier gas was helium, flowing at a rate of 0.33 ml/s. For identification and characterization of the materials contained in the individual GC peaks, an in-house-produced microcapillary fraction collector was used. The compounds thus separated were dissolved in chloroform, and analyzed by infrared spectrophotometry in the range 2.5 to 16 μm .

Preliminary infrared examination was also performed on samples of the liquid before its fractionation by gas chromatography. Such samples contain large amounts of cyclohexene (unreacted material). Consequently, in these cases cyclohexene was also used as the reference material, thus allowing us to obtain ir spectra representative of the reaction products but without having to perform any preliminary separations.

Quantitative determination of the concentrations of the components was based on the areas of the chromatographic peaks. A calibration curve was obtained using known amounts of pure substances and it was found that the same linear curve was applicable to the various components. The percentage conversion (see Fig. 1) is defined as the ratio between cyclohexene con-

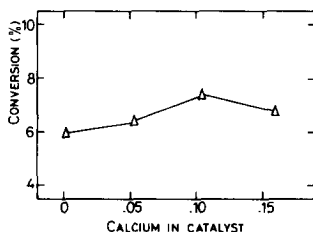


FIG. 1. Conversion of cyclohexene: effect of calcium content in the catalyst. Calcium in catalyst is expressed as the mole ratio $\text{Ca}/(\text{Ca} + \text{Ag})$.

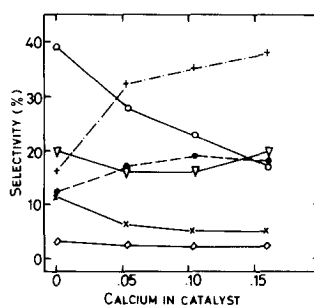


FIG. 2. Selectivity of catalysts toward cyclohexene oxidation products: effect of calcium content in the catalyst, expressed as the mole ratio $\text{Ca}/(\text{Ca} + \text{Ag})$. \circ , Cyclohexene oxide; ∇ , 2-cyclohexene-1-one; \times , 1,6-hexanedial; $+$, 1-cyclopentene-1-carboxaldehyde; \bullet , unidentified product (peak 5); \diamond , CO_2 .

sumed and cyclohexene in the feed $\times 100$ and the percentage selectivity for any given product (see Fig. 2) as the molar ratio between this product and the consumed cyclohexene $\times 100$. The calculations were based on measurements of flows and concentrations in inflowing and outflowing streams.

The gaseous part of the reaction products was analyzed by using a 180-cm GC column maintained at 333 K, and packed with either Porapak Q or 5 \AA molecular sieve. The carrier gas was helium, flowing at a rate of 0.5 ml/s.

RESULTS AND DISCUSSION

Products and Reaction Paths

The chromatograms of the liquid part of the product always comprised six peaks. These are identified in Table 2. The areas of the peaks varied when catalysts with various calcium content were used, but the retention times remained unchanged. Peak 1 refers to unreacted cyclohexene and the other five to products resulting from the reaction. Two of these products were identified unambiguously, as the ir spectra of the individual chromatographic peak fractions were identical with the corresponding spectra of original samples of the pure compounds. These two are cyclohexene oxide (peak 2), and 2-cyclohexene-1-one (peak 4).

TABLE 2
Liquid Components in the Product Stream

Peak No.	Retention time ^a (s)	Identification
1	84	Cyclohexene
2	168	Cyclohexene oxide
3	264	1-Cyclopentene-1-carboxaldehyde
4	402	2-Cyclohexene-1-one
5	684	Unidentified
6	810	1,6-Hexanedial

^a For the experimental conditions used, see the Experimental section.

The nature of two other products was deduced from characteristic absorption bands in the spectra of the corresponding chromatographic peaks. The spectrum corresponding to peak 3 indicated the presence of an aldehydic group conjugated to an olefinic bond (absorption bands at 2720, 1680, and 1625 cm^{-1}). The spectrum corresponding to peak 6 indicated the presence of a nonconjugated aldehydic group (absorption bands at 2720 and 1725 cm^{-1}) and showed no signs of an olefinic bond. It is recalled that in the liquid-phase oxidation of cyclohexene, through hydroperoxide formation, two of the products that are formed in significant amounts are the unsaturated aldehyde 1-cyclopentene-1-carboxaldehyde, and the saturated dialdehyde 1,6-hexanedial. The dialdehyde is formed as a result of the opening of the cyclohexene ring, following oxidation at an allylic carbon atom; at a subsequent stage it closes again, forming the five-carbon-ring unsaturated aldehyde (13). The abovementioned spectroscopic results indicate that a similar reaction may have taken place under the conditions employed in the present work: peak 3 is likely to represent 1-cyclopentene-1-carboxaldehyde, and peak 6 is likely to represent 1,6-hexanedial. Peak 5 was not identified.

Gas chromatography of the gas-phase reaction products showed the presence of a small amount of CO_2 (see Fig. 2). Neither CO nor other carbon-containing gaseous products were detected.

These results lead to the assumption that, in the system investigated, oxidation of cyclohexene proceeds through two simultaneously occurring reaction paths. Path 1 involves attack at the olefinic bond of the reacting cyclohexene and formation of cyclohexene oxide. Path 2 starts by attack at an allylic carbon atom and leads to the formation of the other oxygenated compounds: 2-cyclohexene-1-one and 1,6-hexanedial are probably formed by parallel reaction, and 1-cyclopentene-1-carboxaldehyde probably results from further reaction of the 1,6-hexanedial.

In the present experiments, oxidation of cyclohexene was carried out with a limiting amount of oxygen (molar ratio of O_2 : cyclohexene = 1:5). Under these conditions, and with the various catalysts tested, the conversion of cyclohexene per single pass is in the range of 6–7.5% (Fig. 1). Assuming that only 1 mol of oxygen is consumed per mole of cyclohexene reacted in nondestructive oxidation and 8.5 mol O_2 per mole in total oxidation, this corresponds to an oxygen conversion of approximately 40%.

Figure 2 summarizes the data concerning the selectivity of the process towards the various oxygenated products. Most of the cyclohexene reacted, 97–98%, was mildly oxidized to useful products, and only 2–3% was destructively oxidized to CO_2 . The selectivity toward formation of the epoxide is significant, and reaches 39% of the cyclohexene reacted when the catalyst used did not contain calcium.

These results are dramatically different from the results one obtains with most of the silver catalysts that are not supported by a zeolite, viz., total oxidation to CO_2 . If one assumes that total oxidation is the final step in a series of reactions triggered by the dehydrogenation at the allylic carbon (6), one can deduce from the results of the present work that the zeolitic support turns the silver into a mild catalyst (like bismuth) with regard to this oxidation path, and it makes it promote oxidation only up to the formation of saturated and unsaturated al-

dehydes and ketones. On the other hand, the potency of silver toward the oxidation of the olefinic bond remains and it appears to be capable of promoting the formation of a significant amount of epoxide. Weakening of the oxidation path that starts with the attack at the allylic carbon and favoring the oxidation path deriving from the attack at the olefinic bond is a phenomenon also observed by Van Sickle and Prest (10) in their experiments with olefins adsorbed on zeolites. This seems to be a property of the zeolitic support which manifests itself with various metallic catalysts (cobalt in Ref. (10), silver in our case) and under various experimental conditions (preadsorbed olefin in Ref. (10), reaction in a flow reactor in our experiments).

Calcium Ions in the Zeolitic Catalyst

In the catalysts investigated, Ag is certainly the key element. However, some of these catalysts also contain a fair amount of calcium (up to a Ca/Ag molar ratio of 1:5). The latter is not merely a diluent of the Ag sites, but plays a synergistic role. This effect is brought out in Fig. 1: the conversion of cyclohexene increases with increase of the Ca content. Increase of conversion is observable, although addition of calcium was accompanied by subtraction of an equivalent amount of silver. Presumably the effect would have been more important if calcium had been added to equal amounts of silver, and the negative slope at high concentration of calcium is possibly due to excessive subtraction of silver.

The effect of calcium can be even more clearly appreciated when the selectivity of the catalysts toward the various oxygenated products is considered. Thus, Fig. 2 shows that selectivity for cyclohexene oxide and 1,6-hexanedial decreases when the calcium content increases, while selectivity for 1-cyclopentene-1-carboxaldehyde and for the unidentified peak 5 increases. These results suggest that the reaction path involving oxidation of the olefinic bond is hin-

dered by the presence of calcium, and the reaction path involving oxidation at the allylic carbon is promoted. The observed decrease in the yield of 1,6-hexanedial does not contradict this generalization, as its decrease is more than compensated by the increase of 1-cyclopentene-1-carboxaldehyde that derives from it. One may state that the presence of calcium ions promotes not only the attack at the allylic carbon but also some of the subsequent reactions.

A straightforward result of the exchange of monovalent ions in the zeolite by divalent calcium ions is increased acidity of zeolites, an effect widely used in the preparation of cracking catalysts and thoroughly discussed in the appropriate literature. The abovementioned effects of the calcium content on the distribution of the products of the oxidation of cyclohexene are easily understood if one considers Fig. 2 as a plot against some function of the acidity of the catalyst. The subtraction of hydrogen from an allylic position is known to be associated with the formation of a carbonium ion and to be promoted by acids. The ring closure of 1,6-hexanedial to 1-cyclopentene-1-carboxaldehyde is also known to be promoted by acids. On the other hand, it is worth noting that the fact that zeolites promote epoxidation is not due to their being acidic; promotion of epoxidation occurs in spite of acidity.

Further studies are needed in order to elucidate the mechanism of hydrocarbon oxidation by silver-zeolite catalysts, and in order to find conditions under which selectivity could be improved. Such studies will have to take into account not only the interactions between reactants and catalysts, but also the structural changes occurring in the catalyst at various stages of the process. Such changes have indeed been reported (14-17) to take place.

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