

TEMPERATURE PROGRAMMED REDUCTION AND SPECTROSCOPIC STUDIES OF REDUCTION BEHAVIOR OF Fe/TiO₂ CATALYST

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Fe/TiO₂ catalyst was prepared by incipient wetness impregnation of TiO₂ with aqueous solution of ferric nitrate. The reduction behavior of the catalyst was studied by temperature programmed reduction profiles, Mössbauer spectroscopy, x-ray diffraction and x-ray photoelectron spectroscopy. The results show that the reduction of Fe/TiO₂ was accompanied by a phase transition of anatase to rutile titania. α -Fe₂O₃ was reduced to Fe₃O₄ in the initial reduction stage. Due to the strong support effect of TiO₂, FeTiO₃ was gradually formed as the reduction temperature reached 450°C. Complete reduction to the metallic Fe⁰ particles occurred at temperatures higher than 670°C. The anatase-rutile transition was initiated by the reduced Ti³⁺ ions and led to the formation of TiO_x. At higher reduction temperature, TiO_x migrated to the surface of metallic Fe⁰ particles forming FeTiO_x in the so-called strong metal-support interaction (SMSI) state.

INTRODUCTION

The interaction between metals and their supports has been of particular interest in academic and industrial circles. Due to the phenomenon of strong metal-support interaction (SMSI), as suggested by Tauster *et al.*,¹ the TiO₂-supported group VIII metal catalysts show unusual properties, such as suppressed chemisorption capacities, enhanced activity and higher hydrocarbon selectivity for CO hydrogenation. A comprehensive review of the literature concerning metal-support interactions has been published.² However, the characteristics of SMSI and the mechanism that causes the SMSI phenomena are still obscure.

In the present study, particular interest has been focused on the reduction behavior of the Fe/TiO₂ system using Mössbauer spectroscopy and x-ray diffraction to verify the changes in the composition and structure of the intermediate products during various reduction stages. Mossbauer spectroscopy has been applied to study the different iron phases formed on reduction of iron oxide supported on various oxide supports.³⁻⁸ Reduction of the

Fe/TiO₂ system has also been studied.^{4,5} The origin of SMSI was proposed to be a result of electronic interaction by Tatarchuk and Dumesic.⁴ Nobile and Davis⁵ suggested that the anatase-rutile phase transition and titania grain enlargement are interrelated with the SMSI phenomena during high temperature reduction. In several instances the results appear contradictory. The reduction phenomenon was evidently influenced by the reduction procedure. In order to elucidate the reduction mechanism of the formation of the SMSI state in Fe/TiO₂ catalyst, we investigated the iron composition, structure, morphology and the crystallinity of components formed at different stages of the TPR process.

EXPERIMENTAL

Fe/TiO₂ catalyst was prepared by impregnating Degussa P-25 titania (~50m²/g) with a Fe(NO₃)₂ solution to incipient wetness. The catalyst was subsequently dried at room temperature for two days and left in an oven at 120°C for several hours before storing in a desiccator. The catalyst contains 8 wt% of Fe.

* Dedicated to Professor Wei-Chuan Lin on the occasion of his retirement from National Taiwan University.

The temperature programmed reduction (TPR) profile of the catalyst was monitored by a thermal conductivity detector (TCD), with a mixed gas stream of hydrogen and argon (containing 10% H₂) as a carrier. The flow rate of carrier gas was controlled at 25 cm³/min with an UltraFlo mass flow controller (Vacuum General, Inc.). The temperature of the reactor was increased at a constant rate of 5°C/min controlled by a Eurotherm temperature programmed controller. The output of the TCD signals was simultaneously recorded with an H/P 3393A integrator and a Yokogawa recorder, which also recorded the reactor temperature. The TPR spectrum for Fe/TiO₂ is shown in Fig. 1. Three samples with different extents of reduction were prepared for detailed spectroscopic studies. For samples I, II and III the reduction procedures were followed using the TPR process but the reduction was stopped at 450, 670, and 1000°C, respectively. Each reduced sample was quickly soaked in a 4% Collodion solution (Merck) operating in a dry box under nitrogen pressure to prevent any possible oxidation. After evaporation of the solvent, the dried sample was ground to powders for XRD analysis and pressed into a pellet for Mössbauer spectroscopic measurements.

The ⁵⁷Fe Mössbauer measurements were carried out on a constant-acceleration-type spectrometer using a 50 mCi ⁵⁷Co in rhodium source. Spectrometer calibration was accomplished with a 10 μm α-Fe foil. All spectra were computer-fitted, those found to give the most acceptable fits to

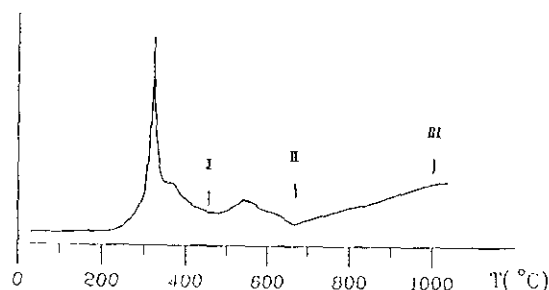


Fig. 1. The TPR profiles of 8 wt% Fe/TiO₂ catalyst. (carrier: H₂/Ar; flow-rate : 30 cm³/min; heating rate : 5C/min.)

the data and satisfactory χ^2 values were used for interpretation. Isomer shifts are quoted relative to α -Fe foil at room temperature.

The x-ray diffraction measurement was performed on a Rigaku D/Max-III diffractometer with nickel-filtered Cu K α radiation. Surface analysis by x-ray photoelectron spectroscopy was performed on the VG Scientific VGS 2000 ESCA spectrometer.

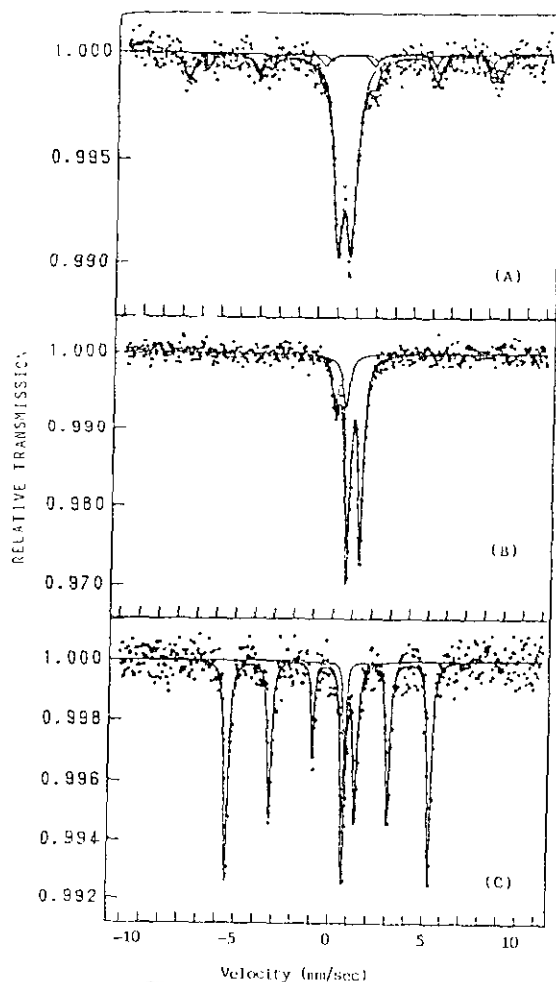


Fig. 2. Mössbauer spectra collected at 25°C of 8 wt% Fe/TiO₂ catalysts which were reduced following the TPR procedures with the reduction stopped at the given temperatures: (A) Sample I, 450°C; (B) Sample II, 670°C; (C) Sample III, 1000°C.

Table 1. Mössbauer spectroscopy parameters of reduced 8 wt% Fe/TiO₂ catalyst.

Sample	Treatment*	Figure	Species	IS,mm/s	QS,mm/s	H,KOe	RA,%
I	RT to 450°C	2(A)	Fe ₂ O ₃	0.369	0.672	-	70
-	-	-	Fe ₃ O ₄ (I)	0.366	-0.197	503	21
-	-	-	Fe ₃ O ₄ (II)	0.609	-0.171	459	9
II	RT to 670°C	2(B)	Fe ³⁺	0.316	0.580	-	26
-	-	-	Fe ²⁺	1.076	0.651	-	74
III	RT to 1000°C	2(C)	Fe ²⁺	1.054	0.668	-	25
-	-	-	α-Fe	0.000	-0.003	329	75

*Reduction of each sample was performed using the same procedures as for the TPR measurement, but the reduction was stopped at the temperatures indicated.

RESULTS AND DISCUSSION

Figure 2 shows the room temperature Mössbauer spectra of the three samples described above. The corresponding spectral parameters determined by the computer fitting procedure are tabulated in Table 1. The sharp quadrupole doublet shown in Fig. 2(A) with an isomer shift of 0.369 mm/s and quadrupole splitting of 0.672 mm/s is indicative of ferric cations, Fe³⁺, which is possibly due to the unreduced Fe₂O₃. The failure to observe the magnetic field was due to the small particle size (< 13 nm). The two sets of sextet spectra with magnetic fields H = 503 and 459 KOe are typically due to the presence of Fe₃O₄. As shown in Fig. 2(B) for sample II, a small amount of quadrupole doublet of Fe³⁺ spectra is observed and most iron-containing species were reduced to Fe²⁺ ions with an isomer shift of 1.076 mm/s and a quadrupole splitting of 0.651 mm/s. For sample III, the computer fitting gave the magnetic hyperfine field of the sextet as 329 KOe, which is due to the presence of zerovalent α-Fe. As shown in Table 1, there was still 25% of the Fe²⁺ remaining unreduced for sample III.

Figure 3 shows the x-ray diffraction spectra of the unreduced 8 wt% Fe/TiO₂ and the three reduced samples. The characters R and A as indicated in Fig. 3(A) and 3(B) represent the XRD peaks due to rutile and anatase forms of titania, respectively. It was clear that before reduction, most titania was in the anatase form (~ 85%) with only ~ 15% in the rutile form, the original form in the Degussa P-25 TiO₂. Traces of Fe₂O₃ are detectable from the peak at

2θ at ~ 33.2. From Fig. 3, reduction of Fe/TiO₂ is found to be accompanied by a phase transition of anatase titania to rutile form. Although there was hardly any detectable Fe₃O₄, the arrows (↓) in Fig. 3(B) indicate features that might be ascribed to traces of such species. With a continued increase of the reduction temperature, FeTiO₃ (FeO·TiO₂) and FeO were formed as evidenced by the peaks indicated with * and + in Fig. 3(C) for sample II. Strong signals due to α-Fe crystallites [peaks with ↑ in Fig. 3(D)] were observed only for sample III. At this stage, the reduced catalyst exhibited very good crystallinity as evidenced by sharp XRD peaks. All anatase titania were transformed to the rutile. Considerable amounts of FeTiO₃ and FeO were still detectable in the sample III. Other peaks are difficult to identify precisely, but they are likely to be due to TiO_x and FeTiO_x, the compounds formed by interaction between Fe and TiO_x.

It is well-known⁹ that titania becomes partially reduced in atmospheres of hydrogen to form surface Ti³⁺ ions associated with one or two anionic oxygen vacancies. The presence of Ti³⁺ defect centers could provide sites at which nucleation of the rutile phase occurs and a rapid diffusion creates a highly chaotic state. The migrating species of TiO_x encounters the reduced iron particles which are stabilized by forming a mixed surface oxide:⁵ Fe + TiO_x → FeTiO_x.

According to the Mössbauer measurements, sample I was composed of 70% Fe³⁺ and 30% Fe₃O₄. The assignment of Fe³⁺ to the unreduced Fe₂O₃ was confirmed by the

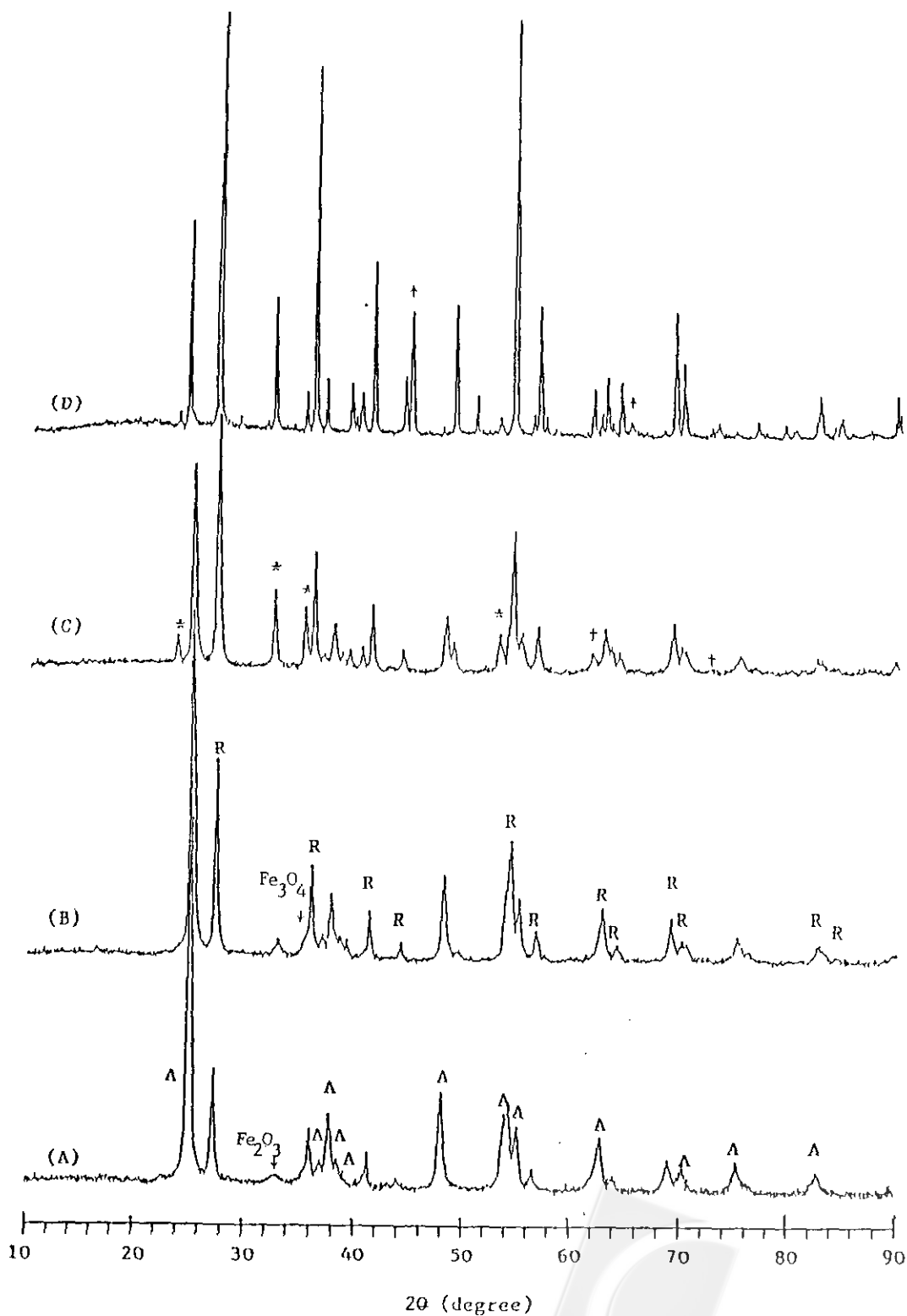


Fig. 3. XRD spectra of 8 wt% Fe/TiO₂: (A) unreduced sample; (B) Sample I; (C) Sample II; (D) Sample III.

XRD spectra. In sample II, the measured 74% of Fe²⁺ should be due to the presence of FeO as well as FeTiO₃ which was also verified by the XRD spectra. There remained 26% of Fe³⁺ unreduced in sample II, but no XRD peaks were observed to provide the compound formula. Sample III was found with 75% α -Fe and 25% Fe²⁺, α -Fe and traces of FeTiO₃ were seen in the XRD spectra. The results of Mössbauer and XRD are in fairly good agreement.

Fig. 4, 5 and 6 are the x-ray photoelectron spectra (XPS) of the electrons of Ti(2p), Fe(2p) and O(1s), respectively. Again, spectra (A), (B) and (C) in each figure correspond to samples I, II and III. According to Fig. 4 and 5, although the binding energies of electrons in both Ti(2p) and Fe(2p) only exhibit subtle differences in the chemical shifts for the three samples, the higher reduction temperature resulted in the lower binding energy. This implies that simultaneous reduction took place in both iron and titania

during reduction of Fe/TiO₂. The remarkable changes in the XPS of the O(1s) electron as shown in Fig. 6 is not only due to the reduction of iron oxides but also due to the phase transition of titania.

CONCLUSION

Considering the above results and discussion of TPR, XRD, XPS and Mössbauer spectroscopy, it can be concluded that the first peak of the TPR spectra shown in Fig. 1 corresponds to the removal of NO₃⁻ anions from the prepared Fe/TiO₂. The high-temperature-side peak shoulder of the first peak is ascribed to the reduction of Fe₂O₃ to Fe₃O₄. The peak between 450 and 670°C is due to the formation of FeTiO₃. The broad peak appearing after 670°C is due to the formation of Fe⁰. During the reduction process, the Ti³⁺ ions initiate the anatase-rutile phase transition and migration of TiO_x to the Fe⁰ produces FeTiO_x which is responsible for the suppression of the chemisorp-

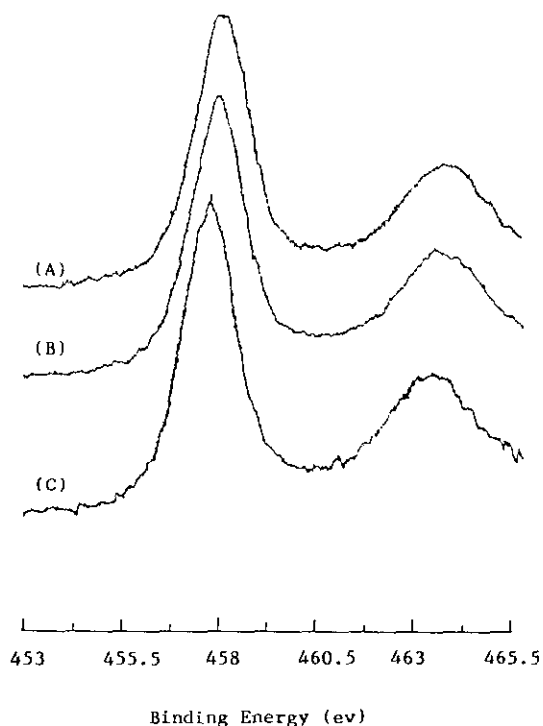


Fig. 4. Ti-2p x-ray photoelectron spectra for Sample I (A); Sample II (B); and Sample III (C).

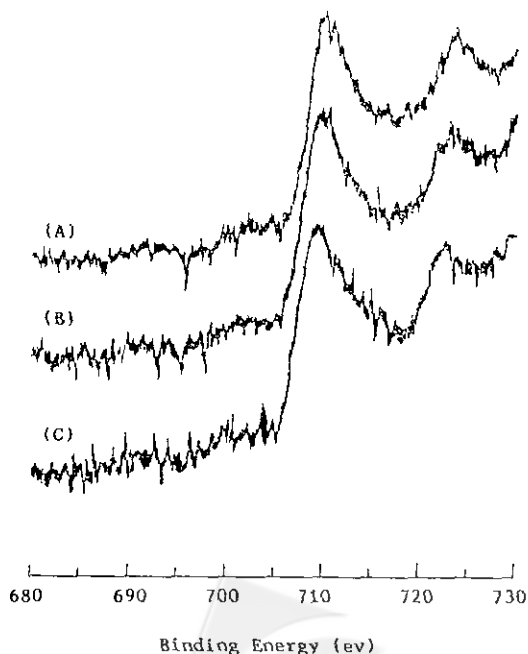


Fig. 5. Fe-2p x-ray photoelectron spectra for Sample I (A); Sample II (B); and Sample III (C).

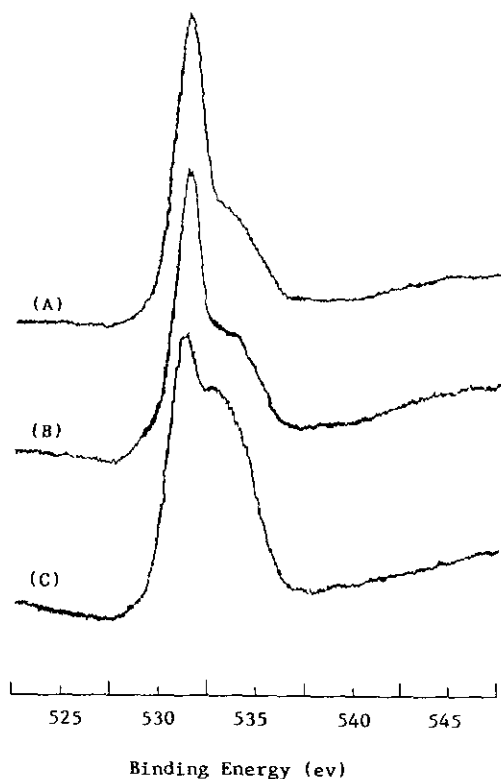
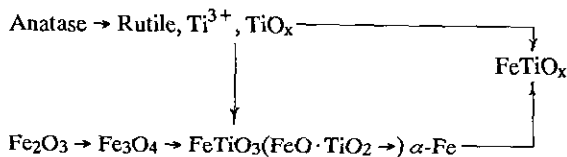


Fig. 6. O-1s x-ray photoelectron spectra for Sample I (A); Sample II (B); and Sample III (C).

tive capability in the SMSI states.

In summary, the reduction of Fe/TiO₂ catalyst proceeds in the following sequence:



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Key Word Index-

Fe/TiO₂; TPR; XRD; XPS; Mössbauer spectroscopy.

REFERENCES

1. Tauster, S.J.; Fung, S.C.; and Garten, R.L. *J. Amer. Chem. Soc.* **1987**, *100*, 170.
2. Stevenson, S.A.; Dumesic, J.A.; Baker, R.T.K.; and Ruckenstein, E., *Metal-Support Interactions in catalysis, Sintering and Redispersion*, Van Nostrand Reinhold, New York, **1987**.
3. Amelse, J.A.; Butt, J.B.; and Schwartz, L.H. *J. Phys. Chem.* **1978**, *82*, 558.
4. Tatarchuk, B.J.; and Dumesic, J.A. *J. Catal.* **1981**, *70*, 308, 323, 335, and 433.
5. Nobile, Jr. A.; and Davis, M.W. *J. Catal.* **1989**, *116*, 383.
6. Clausen, B.S.; and Topsøe, H. *Appl. Catal.* **1989**, *48*, 327.
7. Pijolat, M.; Perrichon, V.; and Bussiere, P. *J. Catal.* **1987**, *107*, 82.
8. Stevenson, S.A.; Goddard, S.A.; Arai, M.; Dumesic, J.A. *J. Phys. Chem.* **1989**, *93*, 2058.
9. DeCanio, S.J.; Apple, T.M.; and Dybowski, C.R. *J. Phys. Chem.* **1983**, *87*, 194.

