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NEW CATALYSTS FOR THE INDIRECT LIQUEFACTION OF COAL. SEMI-ANNUAL TECHNICAL REPORT

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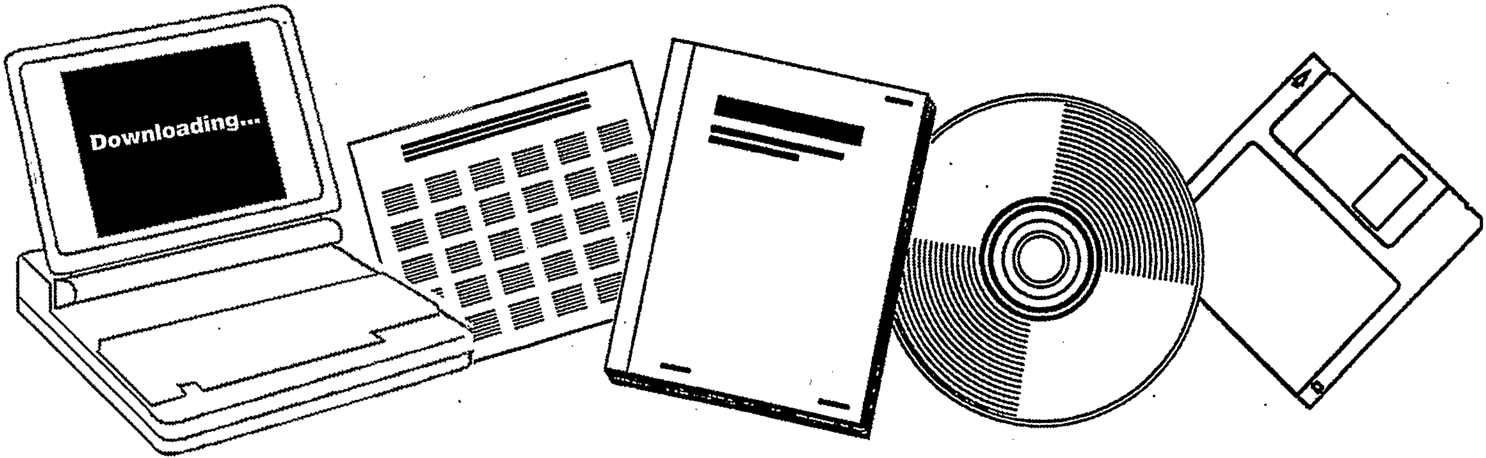

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NEW CATALYSTS FOR THE INDIRECT LIQUEFACTION OF COAL

Semi-Annual Technical Report for Grant No. DE-FG22-80PC30228

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Submitted with proposal in response to Program No. FE-NPI-81-002

by

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Abstract

The synthesis and characterization of two series of supported metal compounds has been achieved during the initial period of grant support. These potentially catalytic materials were prepared from transition metal carbonyls and both simple oxide and zeolite supports by a newly-developed synthetic procedure; spectroscopic and thermogravimetric techniques have been employed for characterization. Evaluation of the ability of some of these materials to catalyze the hydrogenation of carbon monoxide has been completed. Product distributions which are significantly different from those which are obtained by using conventionally prepared catalysts are produced with some of these new materials.

New Catalysts for the Indirect Liquefaction of Coal

During the first six months of the grant period significant progress has been made toward meeting the overall objective of the research proposed in the application under Program No. NPI-80-001. This objective is to develop new, efficient, product selective catalysts for the indirect liquefaction of coal. Specifically, research has been directed toward the development of new materials which will selectively catalyze the production of both new and currently used fuels from synthesis gas (carbon monoxide and hydrogen) mixtures. These potentially catalytic materials, which are supported transition metal compounds, have been synthesized by procedures developed in our laboratory; some have been characterized by a variety of physical techniques and a few have been evaluated for catalytic ability. Some correlations between catalyst structure and catalytic ability have been drawn. The completed and projected research may conveniently be discussed in three separate areas, viz. 1. Synthesis, 2. Characterization studies and 3. Catalytic activity.

1. SYNTHESIS

Most of the efforts in this area have been expended toward the synthesis of two series of supported iron compounds. These series may be considered on the basis of the different supports employed, viz. simple oxides or zeolites. Some cobalt and iron/cobalt mixtures on zeolites have also been prepared. All compounds were prepared by using metal carbonyls as the source of the metal component in a carefully designed and controlled extraction procedure which has been developed in our laboratory(1). This procedure is different from that used previously by researchers to prepare potentially active catalytic materials containing supported metal compounds. The procedure may be conducted in the presence of air or an inert gas, such as dry N_2; usually a dried, de-gassed non-polar solvent is employed as the extracting medium. The developed procedures are similar for the synthesis of each potential catalyst, however, the solvent and reaction times vary with the carbonyl, support used and anticipated weight percent metal loading.

(a) Oxide-supported iron compounds. This series consists of iron on the basic oxides MgO, ZnO, TiO_2 and ThO_2 and the acidic oxides Al_2O_3 and SiO_2. These materials were prepared from $Fe_3(CO)_{12}$ and the oxides using tetrahydrofuran (THF) as the extracting medium for the carbonyl. Metal loadings (as determined spectrophotometrically and/or by atomic absorption spectroscopy) are approximately 12-16%, see Table 1. It should be noted that a few of these materials were prepared prior to the grant period; during the past six months the synthesis of the series was completed. The as-prepared compounds are designated AR; materials prepared from these by heating in air at 500°C for 15 hours are designated 500°. The preparation of a series of samples prepared from $Fe(NO_3)_2 \cdot 9H_2O$ and the oxides by incipient wetness techniques will be completed during the next six months; these samples are for comparison with the newly-synthesized compounds.

(b) Zeolite-supported compounds. Two series of zeolite-supported iron compounds with varying weight percent loadings have been prepared. The zeolites used were ZSM-5 and 13X; the pore diameter for the former is ~6Å, for the latter, ~13Å. These materials were prepared from $Fe_3(CO)_{12}$ and the supports using cyclohexane as the extracting medium for the carbonyl; metal loadings were determined spectrophotometrically (see Table 2). During the next six months, similar series of iron/NU-1, iron/mordenite and ruthenium/ZSM-5 materials will be prepared. These series, together with those already synthesized, will enable the relationship between metal type and location and pore structure to be investigated. It is anticipated that similar procedures will be employed for the preparation of these series. Some "conventional" zeolite-supported iron catalysts will also be prepared for comparison. Other zeolite based materials which have been recently prepared include 20% Co/ZSM-5; 20% Co/NU-1 and 10% Fe-10% Co/ZSM-5. The bimetallic catalyst was prepared by an initial reaction between the support with $Fe_3(CO)_{12}$ followed by reaction with $Co_2(CO)_8$ using cyclohexane as the extracing solvent for both reactions. It does not appear that the second reaction results in loss of the metal component from the first reaction. It is planned to synthesize the bimetallic catalyst with the iron and cobalt deposited on ZSM-5 in reverse order and similar materials with both orders of deposition of the metals for the other zeolites mentioned above. Attempts to co-deposit the metals together will also be made during the next six months.

2. CHARACTERIZATION(2)

All synthesized materials are analyzed for weight percent metal by spectrophotometry and/or atomic absorption spectroscopy. Characterization techniques which have been used or will be used in the future include infrared spectrometry (IR), X-ray powder diffractometry (XRPD), electron spectroscopy for chemical analysis (ESCA, XPS), ion-scattering spectrometry (ISS), secondary ion mass spectroscopy (SIMS), scanning electron microscopy (SEM), Mossbauer spectroscopy (MS) and thermogravimetric analysis (TGA). Characterization of the prepared materials is currently in progress; data obtained during the first six months of the grant period will be presented. It is anticipated that characterization of the materials to be prepared during the next six months will proceed as suitable quantities of analyzed samples become available.

(a) Oxide-supported iron compounds. Some of the as-prepared (AR) samples have been characterized by spectroscopic techniques, see Table 1. It is concluded that the materials contain both Fe^{2+} and Fe^{3+} as oxides on the support surface (ESCA, MS). The Fe/MgO system will be discussed in some detail as illustrative of the data obtained and conclusions reached. Figure 1a shows an X-ray photoelectron spectrum (XPS) for Fe 2p of the Fe/MgO material. The Fe $2p_{3/2}$ peak shape (binding energy ~710eV) and distinct band at ~719eV indicate the presence of Fe^{2+} and Fe^{3+} respectively. Figure 2a shows the O 1s spectrum of the same sample. The doublet structure indicates the presence of two types of oxygen atoms. By comparison with reference compounds (MgO support and Fe_2O_3), it is concluded that the 532eV band is associated with the oxygen of the support, O_S, while the 530eV band is due to oxygen of the iron oxide, O_{Fe}. Sputtering (Ar^+, 10 minutes, estimated penetration ~100Å) does not change the band positions but does alter their relative intensities; the O_{Fe} band increases in intensity relative to that of O_S. This may indicate a "banding" of the iron oxides below the surface. (Such banding has been noted earlier for some iridium and ruthenium/alumina extrudate materials prepared by similar procedures to those employed in this work(1)). For the sputtered sample, the Fe 2p scan still suggests the presence of Fe^{2+} and Fe^{3+}. MS confirms the presence of iron oxides on the support surface whereas XRPD detects only the support, suggesting the iron oxides are highly dispersed and of small particle size (< 50Å). Similar conclusions have been reached for the other AR samples studied (see Table 1). Calcination of the materials in air at 500°C results in significant changes in their appearance and physical properties (see Table 1). XRPD data suggests that this treatment results in the formation of a layer of larger particle-sized iron oxides, e.g. α-Fe_2O_3 or Fe_3O_4 and/or compound formation between the iron and the support, e.g. $MgFe_2O_4$, $ZnFe_2O_4$ for the Fe/MgO and Fe/ZnO systems respectively. Figures 1 and 2 show XPS spectra for the calcined and calcined-sputtered samples of the Fe-MgO system. From the Fe 2p spectra it is concluded that Fe^{2+} and Fe^{3+} are present in both samples and from the O 1s spectra (relative ratio O_{Fe}/O_S that the $MgFe_2O_4$ formed by reaction between the iron and the support is present as a surface layer possibly resulting from a migration of the iron component to the surface during calcination and reaction. The formation of layers of iron containing species for the other materials (see Table 1) is also concluded from XPS spectra for calcined and calcined-sputtered samples. Work is continuing to complete spectroscopic characterization of the other prepared and treated samples in the series. TGA studies demonstrate that reduction of both the as-prepared and calcined materials occurs in flowing H_2 in the temperature range 350-450°C; materials recovered from preliminary evaluations of catalytic ability have been shown to contain Fe_5C_2 for the Fe/Al_2O_3 catalysts and both Fe_5C_2 and Fe_3C for the Fe/SiO_2 catalysts (XRPD).

(b) Zeolite-supported compounds. Some of the as-prepared zeolite-supported iron materials have been characterized by spectroscopic techniques, see Table 2. The approach to the characterization has been similar to that described for the oxide-supported materials and only conclusions together with some representative data will be presented due to limitations on space. For the Fe/ZSM-5 series, it is concluded from XRPD and ESCA that for the lower loadings (<7.9%), the as-prepared materials consist of small particle-sized (<50Å), highly dispersed iron oxides on the support surface. Above 7.9%, XRPD is able to detect larger particle-sized iron oxides on the surface. For all samples, XPS spectra (Fe 2p) indicate the presence of Fe^{2+} and Fe^{3+}; typical spectra for the 16% Fe/ZSM-5 materials, both as-prepared and calcined samples, are shown in Figures 3 and 4. Sputtering again indicates penetration of the iron component in both oxidation states. For the O 1s spectra, both support oxygen, O_s, binding energy ~532eV, and iron oxide oxygen, ~530eV, are detected in AR and calcined materials. In the AR samples, the iron is not all present as an iron oxide since the O_{Fe}/O_S relative ratio decreases on sputtering, (Figures 4a, 4b) whereas the Fe/Si ratio obtained from ISS for AR and AR sputtered samples increases. It is concluded that the iron is present on the surface as an oxide, but penetration into the support results in interaction between the iron and the support. For the calcined samples, Fe 2p XPS spectra indicate the presence of both Fe^{2+} and Fe^{3+} (Figures 3c, 3d); O 1s spectra (Figures 4c, 4d) and the O_{Fe}/O_S ratio suggest larger particle-sized iron oxides on the surface, (also confirmed by XRPD), i.e. dispersion of iron oxides is decreased on calcination. In order to further investigate the nature of the iron-support interaction in the Fe/ZSM-5 materials, ISS and ESCA techniques have been employed for the characterization of the prepared series with weight percent iron ranging from 1.6% to 20.2% (see Table 2); Figure 5 shows the results obtained for this series(3). All ISS and XPS spectra were obtained for sputtered samples, using Ne^+ for ISS and Ar^+ for XPS. The Fe/Si ratios graphed in Figure 5 show that as the weight percent of iron increases to 7.9%, the coverage of the ZSM-5 increases at a rate which is proportional to the loading. This indicates that the size of the iron particles in the 0-7.9% range is approximately constant. After 7.9%, the decrease in Fe/Si slope suggests the formation of larger iron-containing crystallites; XRPD confirms this conclusion. If the iron is being deposited only on top of the support, it is expected that as the weight %Fe approaches zero, the Fe/Si ratio should also tend to zero. However, Figure 5 shows Fe/Si ratios of zero when iron concentrations are in the region of 0.66 to 0.85% by weight. Such behavior could be the result of two factors. First, a "screening effect" on the elements analyzed by adsorbed species could cause discrepancies in concentrations as measured by ISS and ESCA. This factor is expected to be minimized by the reliance on data which were obtained after sputter removal of such adsorbed species. Second, some of the iron could be shielded from observation because of its location within the inner cavities (pores) of the zeolite. It is estimated that if one Fe atom per unit cell is incorporated into the zeolite structure or adsorbed within the ZSM-5 pores, it will constitute approximately 1% by weight of the material. XPS data for the 1.6% Fe material would be expected to be strongly influenced by this incorporated iron, and as the iron concentration is increased, smaller interactive effects would be noticed as a result of the additional iron. As a result of this incorporated iron, activity and selectivity of the catalyst would be altered. ISS data for 300° calcined and 300° reduced Fe/ZSM-5 materials, weight %Fe, 1.6-7.9%, are shown in Figure 6. The Fe/Si ratios for these materials are approximately equal and approximately three times smaller than the as-received materials; this observation is indicative of an increase in particle size of the iron-containing species on heat treatment and is consistent with observations previously made for both zeolite and oxide-supported materials. It should be noted that the Fe/Si ratio reaches zero when the weight %Fe is similar to that for the as-prepared (AR) samples, which may suggest that the "incorporated" iron is still strongly associated with the zeolite. Further investigations are underway and planned for the future, for example, the series of Fe/13X materials with weight percent iron ranging from 1.4 to 17.4% has been prepared and will be investigated by ISS and ESCA techniques as described for the Fe/ZSM-5 series. Ratios of Fe/Si will be obtained and plotted in a similar manner to those in Figure 5. It is anticipated, that if our preliminary conclusion concerning incorporation of iron into the zeolite cavities is correct, the Fe/Si ratio may reach zero at a higher weight percent iron for the 13X series than that obtained for the ZSM-5 series (pore diameters: 13X, 13Å; ZSM-5, ~6Å). Such data should provide more information concerning the structure of zeolite-supported catalysts and should be important in making correlations between catalyst preparation, structure and activity. XPS spectra for used samples of 16% Fe/ZSM-5 are shown in Figures 7 and 8. The O 1s spectra (Figure 7) indicate that complete reduction from the oxide has been effected for the AR sample whereas incomplete reduction occurs for the larger particle-sized oxides obtained after calcination at 300° or 500°C. The C 1s spectra (Figure 8) show the presence of different carbides for the AR used or calcined used samples; XRPD indicates Fe_5C_2 for the AR used sample and Fe_5C_2, Fe_2C, Fe_3C and some unreduced iron oxides for the calcined materials. It should be noted that products from the CO/H_2 reaction obtained from microreactor studies are different for the AR and calcined catalysts, see section 3 and Table 3.

Studies correlating the electronic structure of the supported metal with catalytic activity are also an important aspect of the research in progress. Some Co/ZSM-5 and Co/NU-1 materials, (weight %Co ~20) are being studied by ISS and ESCA techniques. Preliminary information suggests that the cobalt is present in both +2 and +3 oxidation states as small particle-sized oxides in the AR form which increase in size on calcination. For the FeCo/ZSM-5 material (10% Fe-10% Co), XPS spectra indicate the metals are both present in the +2 oxidation state suggesting that deposition of cobalt results in reduction of the previously deposited iron. ISS data (Figure 9) show the "layer" formation of the iron and cobalt oxides in this material.

During the next six months the characterization studies will continue in an attempt to provide a thorough understanding of the structure of the supported metal compounds prepared by our developed procedure.

3. CATALYTIC ACTIVITY

The evaluation of catalytic activity for the prepared and characterized materials for the hydrogenation of carbon monoxide will be carried out in a Chemical Data Systems Inc. Series 804 CF-HP (continuous flow-high pressure) microreactor system. This system was ordered shortly after the grant award under the NPI-80-001 program became available (August 1980), however, it was only recently received and installed. Following some initial installation problems we are, at this time, making final chekcs of the system, installing alarm systems and ensuring that ventillation is adequate for safe operation. It is anticipated that we shall be operational for the initial evaluation of catalytic activity of some of our prepared and characterized materials in the near future. In spite of the frustrating delays in setting up the system (through little fault of our own) we have been able to obtain some data through the Pittsburgh Energy Technology Center(2).

(a) Oxide-supported iron compounds. Preliminary investigations of the Fe/Al_2O_3 and Fe/SiO_2 materials have shown that they are active catalysts for the synthesis of gaseous hydrocarbons and olefins from CO and H_2 mixtures. Typical conditions employed: 2/1 H_2/CO gas mixture at 300 psi, flow rate ~20 ml/min, temperature 300-325°. Prior to evaluation, samples were reduced at 400° in H_2 and then carbided at 250° with the 2/1 synthesis gas mixture. The yields of gaseous hydrocarbons from catalysts prepared by our developed synthetic procedure are significantly higher than those for similar materials prepared by incipient wetness or impregnation procedures.

(b) Zeolite-supported compounds. The catalytic activities of the 16% Fe/ZSM-5 materials have been evaluated, see Table 3. The product distribution from the as-prepared (AR) sample differed considerably from that obtained with catalysts prepared by conventional impregnation techniques, i.e. a much lower percent CO_2 was produced (~27% vs 50-60%) and the aromatic fraction of the oil product, as analyzed by FIA, was more than double that obtained by using a "conventional" catalyst. For the 500°C calcined material, the product distribution was similar to that obtained by using a conventional catalyst. It is proposed that this difference in catalytic behavior is due to differences in the chemical and physical nature of the iron on the support and to differences in the distribution and interaction of the iron with the support (see Characterization section, 2).

When our microreactor system becomes operational, we shall initially repeat the evaluation of the oxide-supported and 16% Fe/ZSM-5 iron catalysts for reproducibility and then during the remainder of the grant period evaluate the catalytic ability of the other oxide-supported compounds and the Fe/ZSM-5 materials with different percent iron loadings. Correlations between catalyst structure and activity (especially the aspects of efficiency and selectivity) will be made where justified.

CONCLUSION

In conclusion, research completed during the first six months of the grant period has led to the synthesis and partial characterization of two series of supported metal compounds. These potentially catalytic materials have been shown to have different structures from those prepared by conventional techniques. Preliminary evaluation of catalytic ability for the CO/H_2 reaction for some of these materials has demonstrated that different product distributions are produced, and attempts to correlate catalytic activity with the nature of the catalyst have been made. Further studies are in progress and planned to more fully characterize these new materials and to determine those factors which are important in producing catalysts which give rise to "non Fischer-Tropsch" product distributions in the indirect liquefaction of coal.

REFERENCES

1. G. A. Melson, J. E. Crawford, K. J. Mbadcam, F. R. Brown and L. E. Makovsky, 19th Symposium of the Pittsburgh Catalysis Society, Monroeville, PA (1980).

2. The Principal Investigator acknowledges with gratitude the assistance of personnel at PETC in obtaining some of the data reported.

3. J. M. Stencel, J. R. Diehl, L. J, Douglas, J. E. Crawford and G. A. Melson, Colloids and Surfaces, to be submitted (1981).

Table 1. Oxide-Supported Iron Compounds

Support	Wt % Fe	Form of Fe	
		AR(a,b,c)	500°(a,d)
MgO	12.3	Fe^{2+}, Fe^{3+}/oxide	Fe_3O_4, $MgFe_2O_4$
ZnO	16.4	Fe^{2+}, Fe^{3+}/oxide	Fe_3O_4, $ZnFe_2O_4$
TiO_2	11.9	Fe^{2+}, Fe^{3+}/oxide	α-Fe_2O_3
ThO_2	11.7	(e)	(e)
Al_2O_3	14.0	(e)	α-Fe_2O_3
SiO_2	14.7	(e)	Fe_3O_4. α-Fe_2O_3

(a) AR is as-prepared form, 500° is AR sample calcined in air at 500°C for 15 hours

(b) Data from ESCA and Mossbauer Spectroscopy

(c) XRPD detects support only

(d) Data from XRPD

(e) Not completed

Table 2. Zeolite-Supported Iron Compounds

Support	Wt % Fe	Form of Fe, AR(a)	
		XRPD	ESCA
ZSM-5	1.6	(b)	Fe^{2+}/Fe^{3+} (equal)
	3.0	(c)	(c)
	4.4	(b)	Fe^{3+}, Fe^{2+}
	5.8	(b)	Fe^{2+}, Fe^{3+}
	7.1	(c)	(c)
	7.9	$Fe_3O_4/\gamma\text{-}Fe_2O_3$	Fe^{2+}, Fe^{3+}
	13.8	$Fe_3O_4/\gamma\text{-}Fe_2O_3$	Fe^{2+}, Fe^{3+}
	15.0	(c)	(c)
	16.0	Fe_3O_4	Fe^{2+}, Fe^{3+}
	20.2	$Fe_3O_4/\gamma\text{-}Fe_2O_3$	Fe^{2+}, Fe^{3+}
13X	A series of Wt % Fe of 1.4, 2.7, 3.7, 5.8, 8.8, 11.1, 13.5, 15.3 and 17.4 has been prepared; at this time no characterization data have been obtained.		

(a) As-prepared form

(b) Support only detected

(c) Not completed

Table 3. Catalytic Activity for 16.0% Fe/ZSM-5 Samples

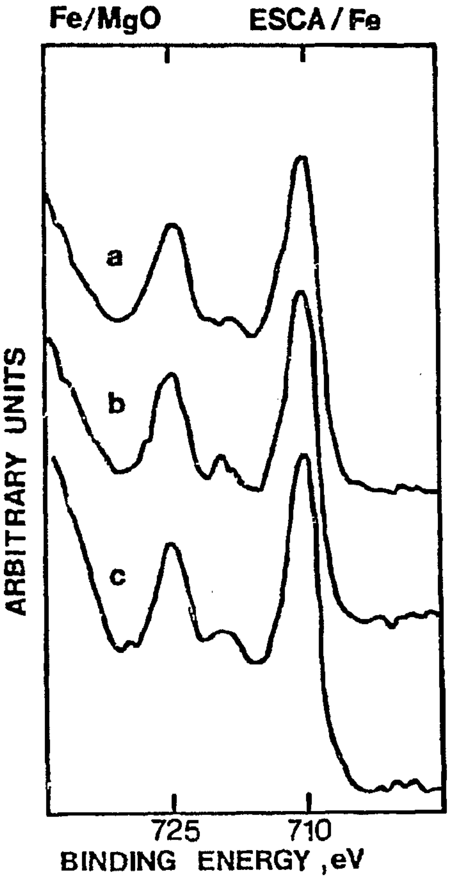
Sample	Temp.	Product Distribution %			H/C distribution %				Conversion %	
	°C	H/C	H_2O	CO_2	C_1	C_2	C_3	Oil	CO	H_2
AR[(a)]	280	29	37	34	41	21	20	19	24	40
	300	32	42	27	40	19	9	32	21	39
300°[(b)]	280	42	37	21	38	24	14	24	24	39
500°[(c)]	280	31	37	32	27	19	15	37	31	49
	300	30	17	53	28	18	11	40	54	62

(a) As-prepared form

(b) AR form calcined in air at 300° for 15 hours

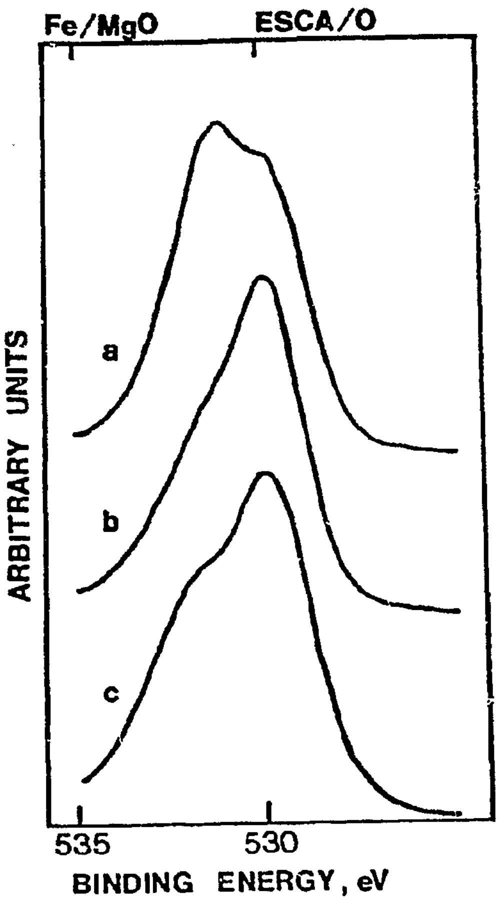
(c) AR form calcined in air at 500° for 15 hours

1.



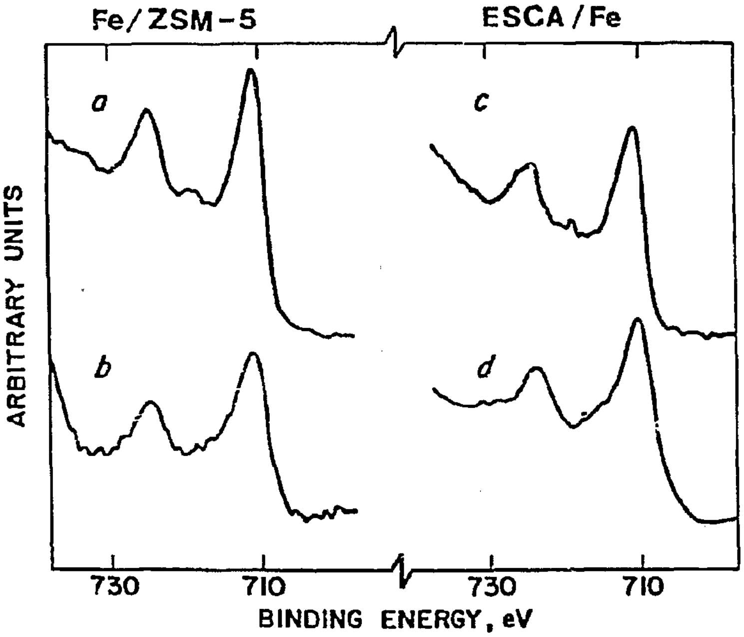
(a) AR
(b) 500 °C
(c) 500 °C, SP Ar$^+$

2.



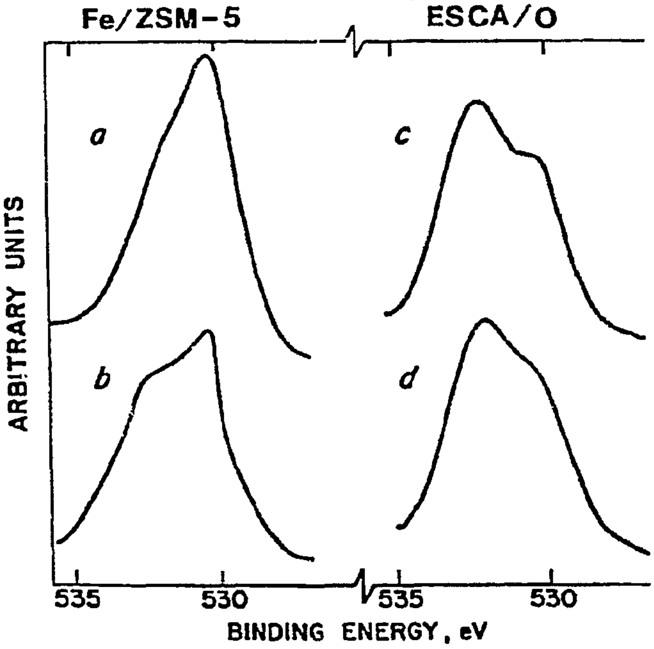
(a) AR
(b) 500 °C
(c) 500 °C, SP Ar$^+$

3.



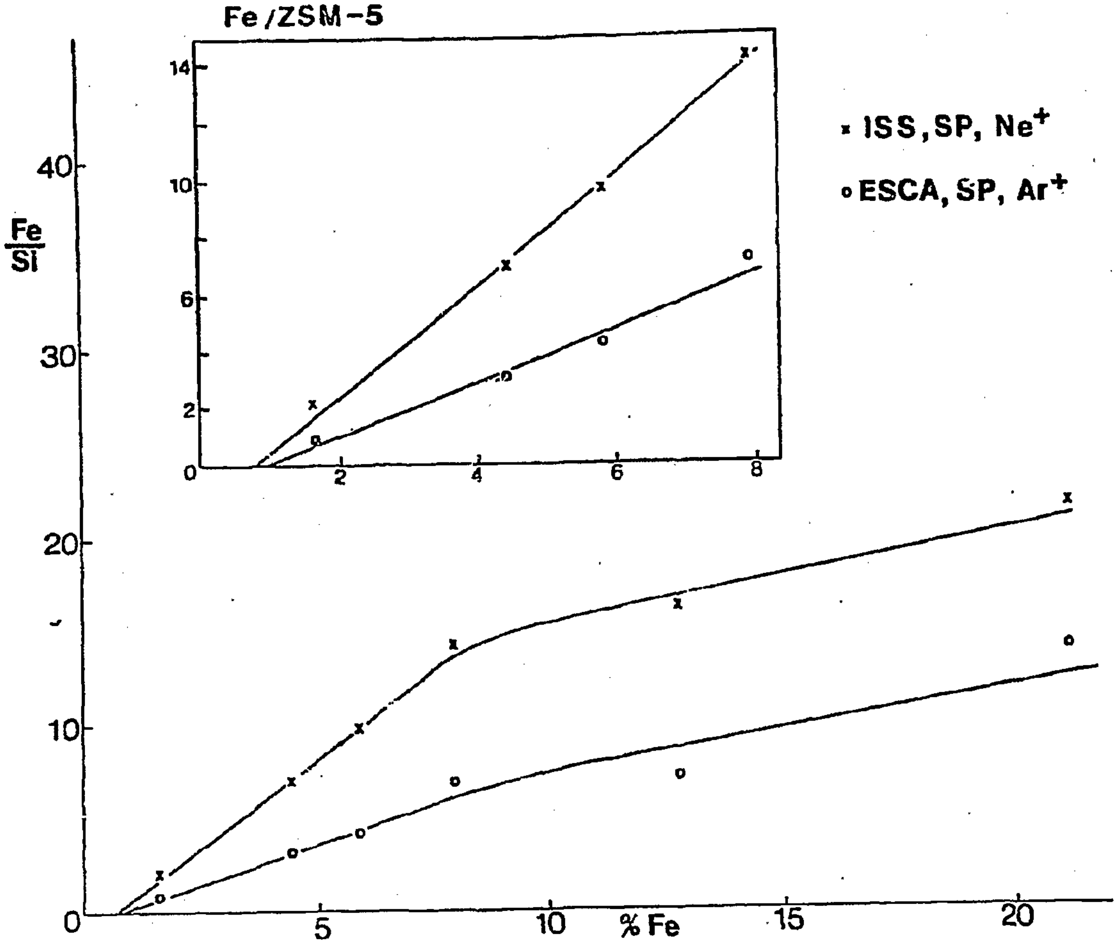
(a) AR
(b) AR, SP Ar$^+$
(c) 500°C
(d) 500°C, SP

4.



(a) AR
(b) AR, SP Ar$^+$
(c) 500° C
(d) 500° C, SP

5.


Fe/ZSM-5
14
10
6
2
0
2
4
6
8
× ISS, SP, Ne$^+$
○ ESCA, SP, Ar$^+$
Fe/Si
40
30
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10
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5
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% Fe
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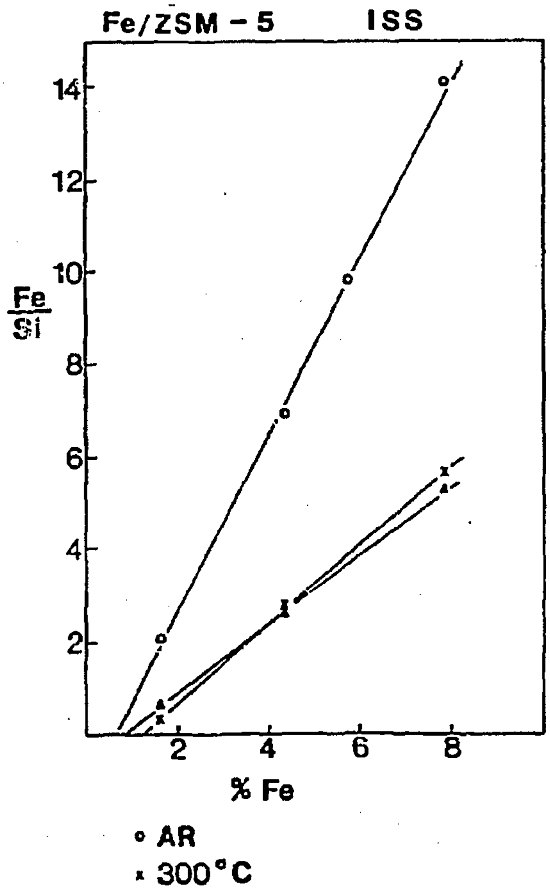
20

6.


Fe/ZSM - 5
ISS
Fe/Si
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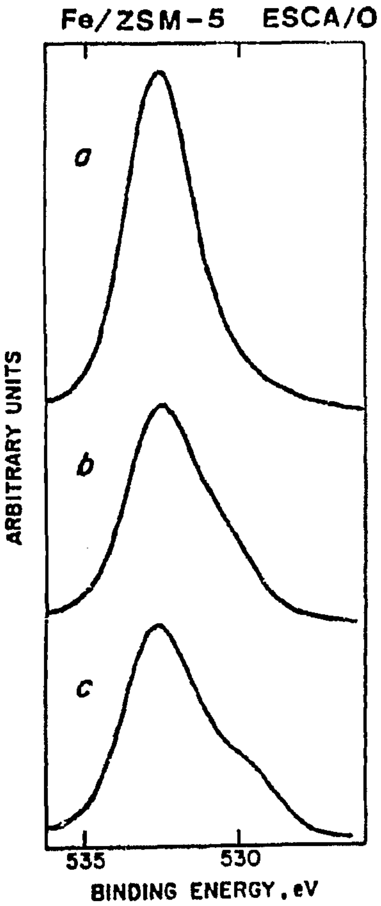
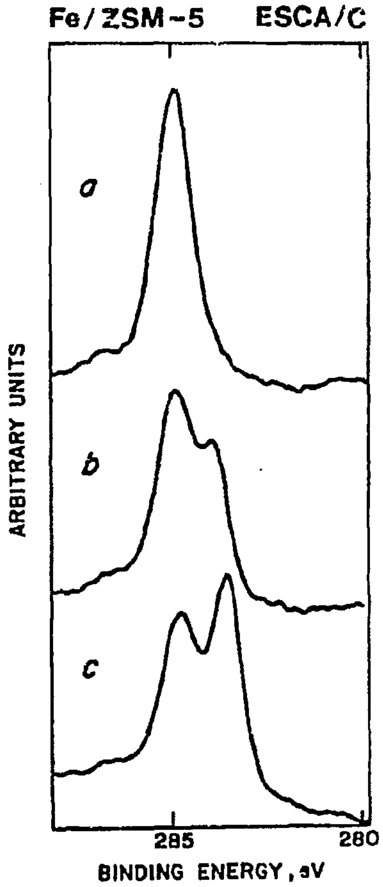
7.



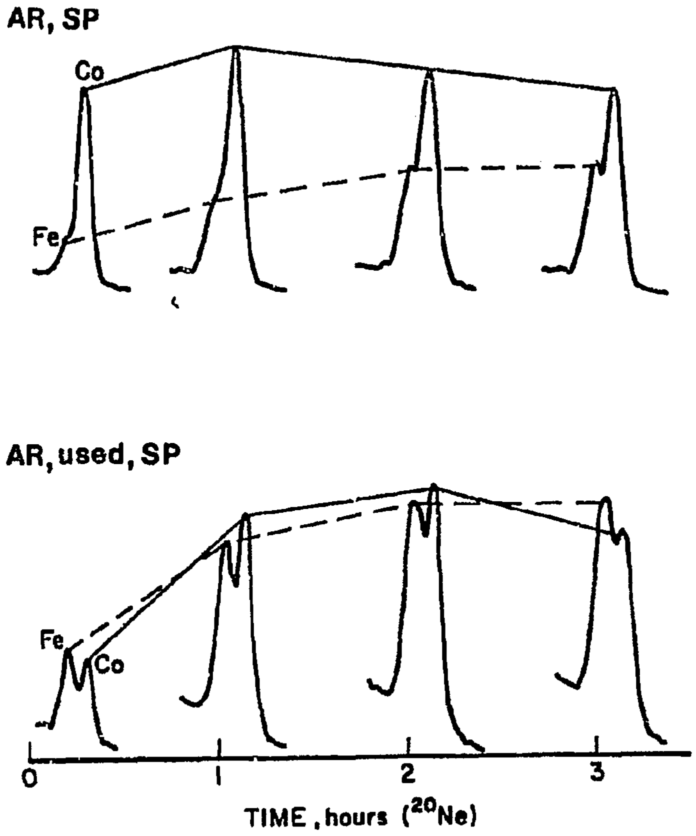
(a) AR, used
(b) 300 °C, used
(c) 500 °C, used

8.



(a) AR used SP Ar^+
(b) 300°C, used, SP
(c) 500°C, used, SP

9.



Fe-Co-ZSM-5
ISS