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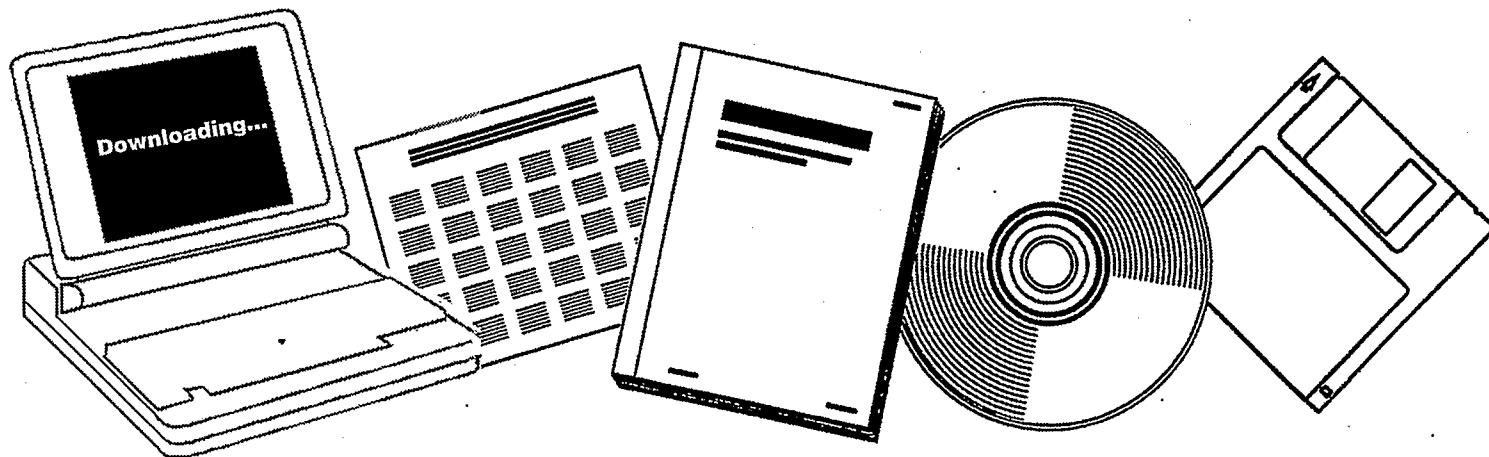
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**CATION PROMOTION EFFECTS IN
ZEOLITE-SUPPORTED F-T CATALYSTS. FOURTH
QUARTERLY REPORT, JUNE 1984-AUGUST 1984**

**PITTSBURGH UNIV., PA. DEPT. OF CHEMICAL
AND PETROLEUM ENGINEERING**

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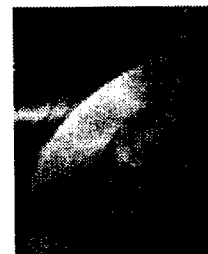
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CATION PROMOTION EFFECTS IN
ZEOLITE-SUPPORTED F-T CATALYSTS

4th Quarterly Report
June 1984 - August 1984

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I. OBJECTIVE AND SCOPE OF WORK

An investigation into zeolite-supported F-T catalysts begun under Grant #DE-FG22-81PC40774 (Office of Fossil Energy, D.O.E.) has produced results which suggest that alkali cations, remaining in a zeolite and serving to neutralize the structure, act to promote higher hydrocarbon formation. It appears that the F-T metal must be highly dispersed throughout the zeolite in the vicinity of these cations for this promotion effect to take place. This effect is also highly dependent upon alkali cation concentration.

The current research involves a study of the promotion effects of the neutralizing alkali cations on CO hydrogenation (under typical F-T conditions) over zeolite-supported Ru catalysts. Ru is a useful, model catalyst for the study of such promotion of this synthesis. First, alkali promotion has been found to have a great effect on product selectivity over Ru. Second, Ru does not form any stable carbides, thereby removing this complicating factor. Third, Ru is relatively easy to reduce to the metallic state. Fourth, Ru is the F-T metal easiest to keep inside zeolite crystallites. Fifth, under typical conditions, there is little oxygenated hydrocarbon formation or skeletal isomerization of the hydrocarbons over Ru. Thus, the neutralizing cations in the zeolite support should affect CO hydrogenation over Ru possibly by affecting: CO chemisorption, H₂ chemisorption, carbon deposition, catalytic activity, chain growth probability, selectivity for CH₄, selectivity for olefins, and diffusion in the zeolite. Each of these items will be investigated for the catalysts proposed to be studied.

The main objectives of this study are:

1. to develop a better understanding of how neutralizing alkali cations in zeolites can affect F-T product selectivity over a supported metal
2. to illuminate the effect of these cations on

- a. chemisorption properties
 - b. CO disproportionation
 - c. the mechanism of CO hydrogenation
 - d. the deactivation characteristics
3. to elaborate upon the effect of decreasing ionization potential of the alkali cations on the catalytic properties
 4. to investigate the effects of Rb and Cs promotion, studied only superficially in the past.

In order to accomplish these objectives, several series of catalysts have been prepared. These catalysts are mainly zeolite-supported Ru prepared using NaX, NaY, KL, X and Y zeolites containing a range of alkali cations (Cs^+ , Rb^+ , K^+ , Na^+ and Li^+), and a series of dealuminated NaY zeolites. Preparation and characterization of these samples by means of gas volumetry and atomic absorption have been described in a previous quarterly report. Further investigations of surface and catalytic properties are under way.

This investigation should provide a more fundamental understanding of the involvement of alkali cations in determining the catalytic properties of zeolite-supported metals for CO hydrogenation.

II. SUMMARY OF PROGRESS

During this quarter, June 1, 1984, to August 31, 1984, we have focussed our efforts on two main tasks

II-1 CO Hydrogenation

CO hydrogenation have been performed at atmospheric pressure and in the temperature range 220-300°C. The catalysts used were Ru supported on the following zeolites: NaY, LiY, KY, CsY, RbY, HY, NaX and KL. All catalysts have been analyzed by atomic absorption and found to contain 3 ± 0.1 wt% Ru. The following features will be discussed in the next section:

- activity and selectivity
- dependence of the olefin fractions upon the nature of the support
- relationship between the composition of C_4 fractions and the support acidity

II-2 Cyclopropane Hydrogenation

Another microreactor system (see Figure 1) has been constructed for performing cyclopropane hydrogenation over a series of 0.15 wt% Ru/zeolites. The preparation of these catalysts have been described in the 2nd quarterly report.

III. DETAILED DESCRIPTION OF TECHNICAL PROGRESS

III-1 Carbon Monoxide Hydrogenation

The title reaction has been carried out over all the 3 wt% Ru catalysts in a differential stainless steel microreactor using the following experimental conditions: temperature range: 220-300°C, total pressure: 1 atm, $H_2/CO = 1$, total flow rate: 2.4 l/h, catalyst weight: 250 mg, conversion: < 10%.

Under these conditions, all catalysts produced hydrocarbons having 1 to 6 carbon atoms. The main features may be summarized in three points:

- Activity and Selectivity Patterns:

Based on CO conversion in mole/h.kg Ru, relatively small variations in the catalytic activity have been observed. Figure 2a shows a maximum activity for RuNaY. For the time being, no definite answer can be formulated concerning whether this behavior is related to a particle size effect or to a support effect. More accurate explanation may be obtained after completing H_2 and CO chemisorption experiments.

As depicted in Figure 2b, the selectivity for CH_4 formation is essentially the same for all the Y zeolites (35-40%). Therefore it seems

that, provided the zeolite type is conserved, neither the alkali cations nor the acidity has a substantial effect on the product selectivities, at least at atmospheric pressure. Conversely, when NaX or KL are used as supports, lower and higher selectivity in CH₄ are obtained, respectively. In agreement with these results, it has been reported by other workers that RuNaX yields less methane than RuNaY (1). These results have been explained on the basis of a stronger metal-support interaction in the case of RuNaY due to the fact that NaY is more acidic than NaX. However our findings cannot be fully explained in the same terms because RuHY and RuNaY exhibit the same selectivity towards CH₄ in spite of the higher acidity of RuHY.

In order to unravel this problem, more experiments and characterization are planned.

- Olefin Fraction

The C₃ fraction has been selected to compare the olefinic fractions yielded by the various catalysts. This choice was made because, as expected the C₂ fraction is mainly paraffinic and the fractions of hydrocarbons having more than three carbon atoms are complicated by secondary reactions (see below). The ratios of $\bar{C}_3/\Sigma C_3$ obtained at constant conversion (~ 2.5%) are shown in Table 1.

Table 1: $\bar{C}_3/\Sigma C_3$ obtained with 3 wt% Ru Supported Catalysts at ~ 2.5% CO Conversion

Support	NaX	LiY	NaY	KY	RbY	CsY	KL	MgO ^(a)	SiO ₂ ^(b)
$\bar{C}_3/\Sigma C_3$	0.93	0.78	0.78	0.81	0.90	0.88	0.28	0.70	0.29
T(°C)	253	225	239	230	233	235	270	271	263
S(CH ₄)% at 250°C	20				~ 35		70	25	50

(a) 5 wt% Ru, (b) 2.2 wt% Ru

This table shows that the variation of the olefin fraction with the nature of the support is rather complex. The olefin fraction seems to be dependent upon conversion and reaction temperature, as well as the ability of the catalyst to yield higher hydrocarbons. When Y type zeolites are used, both selectivity for C_2^+ (~ 65%) and the fraction C_3^-/C_3 (~ 0.85) are not very much affected by the nature of the alkali cation. In contrast to RuKL, RuNaX yields much more propene and much less methane than RuMY (M = alkali metal). It may be concluded that the hydrogenation ability and that of methanation follow each other and they are highly dependent on the type of zeolite used. Furthermore Ru/MgO and RuSiO₂ follow the same trend, that is, the higher methanation selectivity is accompanied by the higher hydrogenation ability.

- Composition of the C₄ Fraction

The chromatographic analysis procedure used in this work allows one to fully analyze the C₄ fraction. The C₅ and C₆ fractions may also be analyzed in detail, however, the results are less accurate owing to the small quantities of these products. Therefore only the C₄ fraction has been analyzed in detail, while a global analysis has been made for the C₅ and C₆ fractions.

Strong evidence that the primary product (1-butene) undergoes subsequent hydrogenation as well as double bond shift and skeletal isomerization have been obtained. Figure 3a shows that at 250°C, RuHY gives 54% isobutane (based on the total amount of C₄). When this catalyst is further exchanged (after reduction) with a dilute solution of K₂CO₃, the isobutane is no longer obtained. On the other hand, RuRbY yields only very small quantities of isobutane, but, when mechanically mixed with HY, the isobutane content of the C₄ fraction increases to 30%. Therefore, it is concluded that the isobutane is formed by a secondary reaction via a bifunctional mechanism.

Figure 3a shows also that the proportion of isobutane decreases in the order



With the exception of RuHY, all other catalysts are expected to have the same number of acidic sites. This means that the extent of the skeletal isomerization leading to iso-C₄ is not a simple function of the overall acidity of the catalysts. It is believed that the proportion of iso-C₄ is related to the acid strength which may be affected by the nature of the alkali cations present. Further evidence would be provided by acidity distribution measurements. In order to clarify this aspect, a TGA study of ammonia adsorption as a function of temperature will be conducted very shortly. Finally, when supports with very low acidity (SiO₂, NaX, MgO) are used isobutane is detected.

The double bond shift and cis/trans isomerization are known to occur on both acidic and basic sites. Figure 3b shows that 1-butene as well as cis and trans-2-butene are obtained over all catalysts. Moreover the ratio cis/trans is almost constant (~ 1.6) and close to unity indicating that the isomerization takes place on acidic sites probably via carbonium ion (2,3) formation. This is not surprising since it is known that base catalyzed isomerization of 1-butene occurs only at higher temperatures (> 400°C) and yields mainly cis-2-butene.

III-2 Cyclopropane Hydrogenation

Several studies in the literature show that cyclopropane hydrogenation is a good tool to investigate the electrostatic field effect of zeolites (4) which may be affected by the nature and concentration of the neutralizing alkali cations. It has also been shown that PtNaY as well as RuNaY are very active for cyclopropane hydrogenation (5). In order to be able

to achieve low conversions under reasonable experimental conditions, a series of 0.15 wt% Ru on zeolite has been prepared. Preliminary experiments are under way, and this topic will be dealt with in detail in the forthcoming report.

IV - FORECAST OF WORK

During the next quarter

- H₂ and CO chemisorption and BET experiments should be completed;
- TGA studies of ammonia adsorption will be conducted in order to determine the effect of alkali cations on the acid strength of the various catalysts;
- the cyclopropane hydrogenation experiments which have been started this quarter will be continued;
- the CO hydrogenation experiments will be continued. In order to assess the hydrogenation ability of Ru/zeolites under FT conditions, small amounts of ethylene will be added in the CO/H₂ stream at steady state.

References

1. P.A. Jacobs, J. Verdonck, R. Nijs, and J.B. Uytterhoeven, *Adv. Chemistry Series* 178, 15 (1979).
2. J.W. Hightower and W.K. Hall, *J. Amer. Chem. Soc.* 89, 778 (1967); *J. Phys. Chem.* 71, 1014 (1967).
3. J.B. Nagy, J. Harmel, A. Abov-Kais, M. Guelton, and E.G. Derouane, *J. Catal.* 88, 73 (1984).
4. C. Naccache, N. Kaufherr, M. Dufaux, J. Bandiera, and B. Imelik, in "Molecular Series II," J.R. Katzer, ed., Amer. Chem. Soc. Washington, D.C., 1977, p. 538.
5. J.G. Goodwin, Jr., unpublished results.

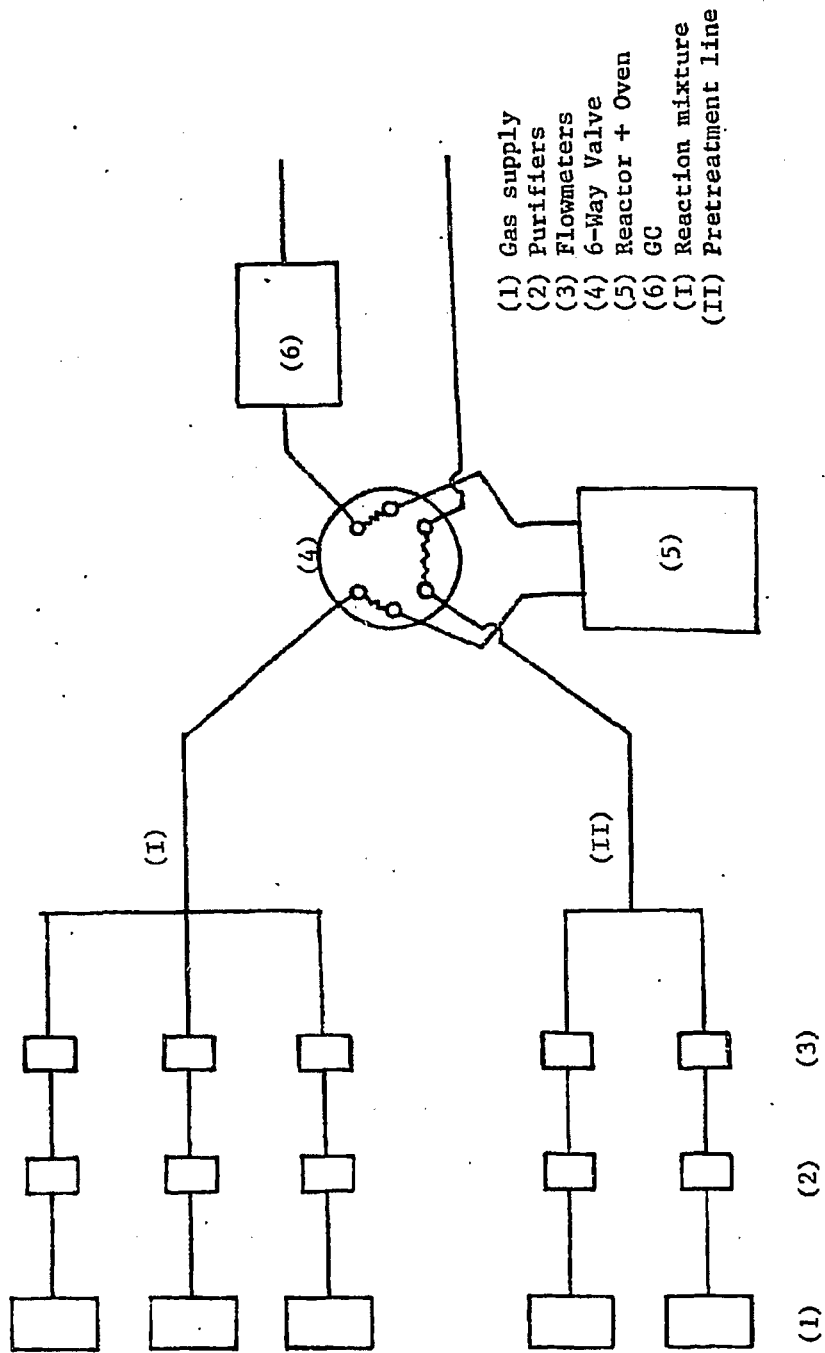


Figure 1: Cyclopropane reaction system.

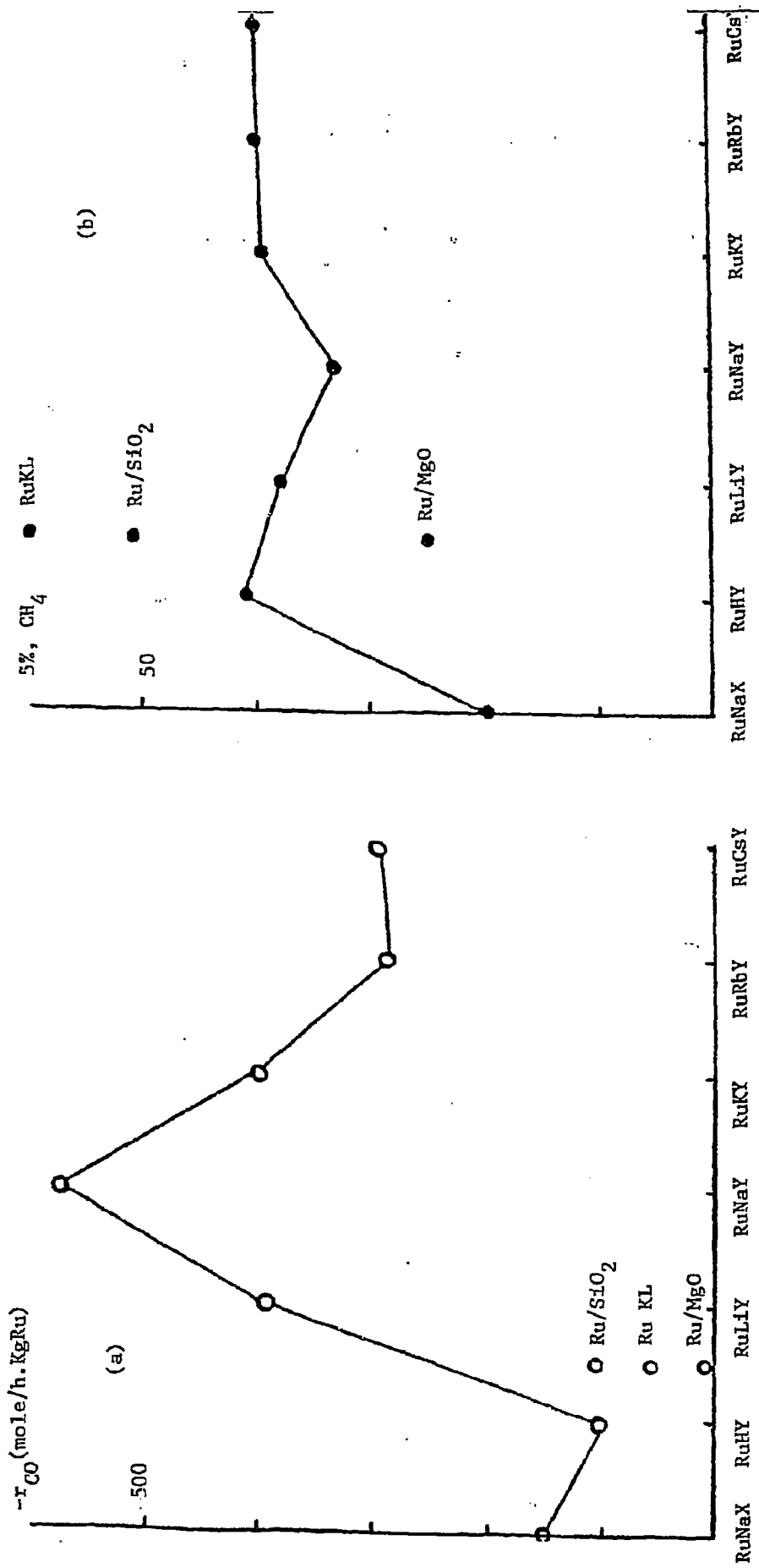
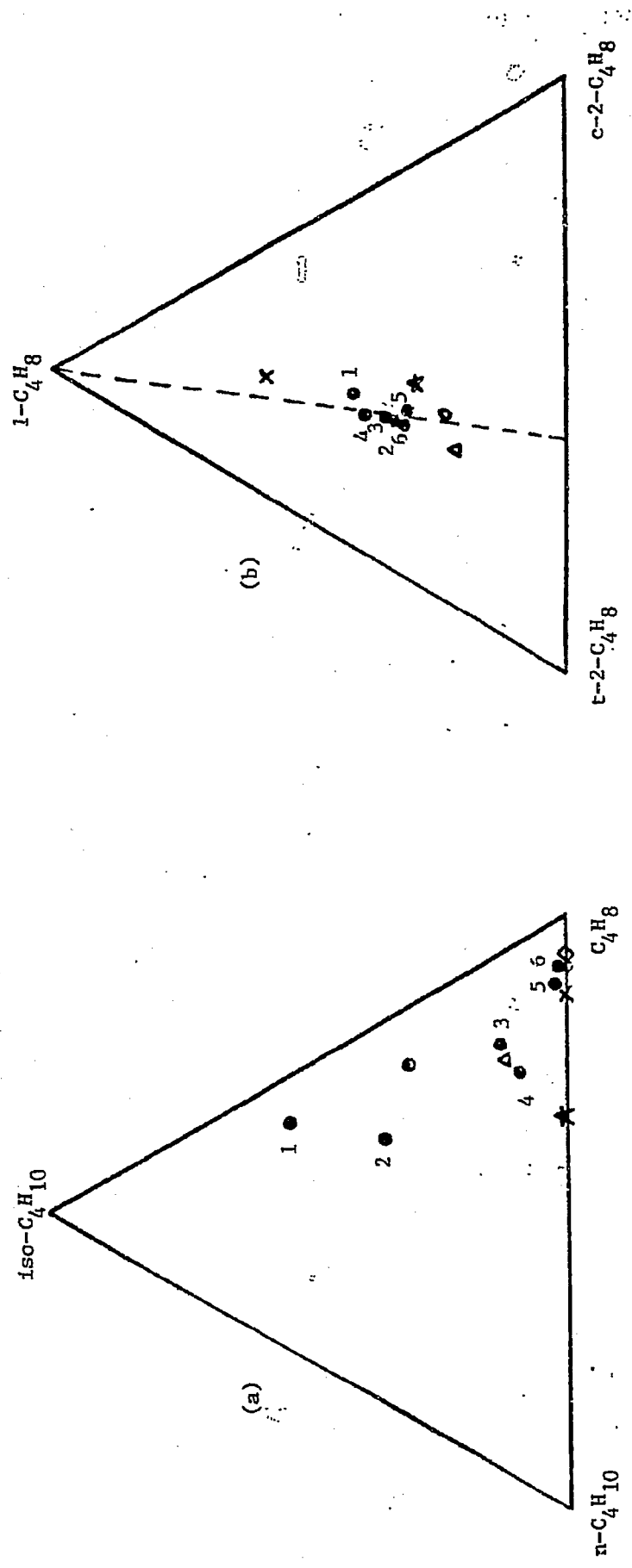


Figure 2: CO hydrogenation over supported Ru. (a) Overall activity (b) Selectivity for CH_4 formation.

Figure 3: C₄ fraction analysis.



- RuMY: (1) RuHY, (2) RuLiY, (3) RuKY, (4) RuNaY, (5) RuCsY, (6) RuRbY
- Δ RuKL, ○ RuNaX, ● RuRbY + HY, ◊ RuHY exchanged with K_2CO_3 , X Ru/MgO, ★ Ru/SiO₂

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