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The Use of MCM-22 as a Cracking Zeolitic Additive for FCC

Avelino Corma[1] and Joaquín Martínez-Triguero

Instituto de Tecnología Química UPV-CSIC, Universidad Politécnica de Valencia, Avenida de los naranjos s/n. 46022 Valencia, Spain

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The catalytic cracking of gasoil has been carried out on a MCM-22 zeolite sample. This zeolite, in agreement with the proposed structure, shows little activity for cracking the large molecules present in the vacuum gasoil feed. However, when it is used as a cracking additive in combination with a USY based cracking catalyst, and its behaviour is compared with that of a ZSM-5 zeolite additive, it is found that MCM-22 produces less total gases, as well as less dry gases, with a lower loss of gasoline than ZSM-5. On the other hand, the propylene to propane and butene to butane ratio is higher in the case of MCM-22, showing a very adequate behaviour within the frame of the production of reformulated gasolines. However, ZSM-5 is more active than MCM-22 and at low rates of addition, ∼3 wt%, ZSM-5 shows a larger effect than MCM-22. In order to see the benefits of MCM-22 as a cracking additive, larger amounts (∼13 wt%) need to be introduced. ZSM-5 gives a higher ratio of protolytic to β-scission cracking than MCM-22, and the steam stability of MCM-22 is quite good, being even higher than that of ZSM-5. Finally, we present a method for testing additives during gasoil cracking which enhances their effects and allows us to show very clearly the cracking behaviour of zeolite additives.

1. INTRODUCTION

Since the introduction of catalytic cracking in 1942, the process engineering and catalyst design have continuously evolved to accommodate the production of the different commercial and environmental demands. This has been particularly so from the point of view of the cracking catalysts which started as amorphous silica-alumina and evolved with time to the use of REY zeolites and, finally, to the REUSY and multizeolite catalysts used today. In this sense, ZSM-5 has been used in recent years as an additive to boost gasoline octane and to increase the yield of propylene at the expense of gasoline yield.

There is no doubt that the Clean Air Act amendments are going to strongly affect the FCC as an important gasoline producing unit. In this direction improvements will point to decreased sulfur, to maximize the octane barrel while keeping a good throughput, and to be flexible enough to increase the production of valuable C_3–C_5 olefins and isobutane, which are desired for the production of oxygenates and alkylated gasoline.

It appears evident that it will be difficult to accomplish all these goals with a simple catalyst formulation, and one may oversee the possibilities of using, besides Y, other zeolites and zeolitic materials, either as the main active cracking component, or, what is more probable, as catalyst additives.

Some attempts have been made to explore the possibilities of zeolites other than ZSM-5 as cracking catalysts. In this way the behaviour of some large pore zeolites such as Beta and Omega have been discussed in the open literature (1, 2). Among them, Beta zeolite appears as more adequate since, while giving some conversion, it increases the production of C_4 and C_5 isoolefins without too much gasoline penalty (2). However, when zeolite Beta is used as an additive, its effect is only seen at relatively high levels of addition (3). After this, it appears that a structure which combines large and medium pore channels can be adequate as a cracking additive to boost octane and to increase the production of C_3 and C_4 olefins.

The recently discovered MCM-22 zeolite has a structure which combines large cavities formed by 12 member rings, with a system of independent 10 member ring channels (4), and this appears as an interesting structure which may combine, just in one zeolite, catalytic properties of 12 and 10 member ring structures.

In this paper we first discuss a strategy to test zeolite additives for gasoil cracking in MAT units, and then the gasoil cracking behaviour and hydrothermal stability of MCM-22 is studied and compared with that of a ZSM-5 zeolite.

2. EXPERIMENTAL

2.1. *Materials*

The catalysts used were: zeolite USY (CBV720 from PQ Zeolites), ZSM-5 (CBV5020 from PQ), and a MCM-22. The latter was synthesized in the following way (5): A synthesis mixture was prepared using hexamethylenimine (Aldrich), silica (Aerosil 200, Degussa), sodium aluminate (56% Al_2O_3 37% Na_2O, Carlo Erba), sodium hydroxide (98% Prolabo), and deionized water. Sodium aluminate and

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[1] To whom correspondence should be addressed.

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sodium hydroxide were dissolved in water. To this solution hexamethylenimine and silica were added with vigorous stirring that was maintained for 30 min. After this, the resulting gel with a composition: $SiO_2/Al_2O_3 = 30$, $OH/SiO_2 = 0.18$, hexamethylenimine/$SiO_2 = 0.35$ and $H_2O/SiO_2 = 45$ was introduced into 60 ml of PTFE-lined stainless-steel autoclaves, rotated at 60 rpm, and heated at 423 K for 7 days. After quenching the autoclaves in cold water, the samples were centrifuged at 10000 rpm, washed and dried at 353 K overnight. Finally the sample was calcined in air at 853 K for 3 h.

The characteristics of the zeolites used in this work are given in Table 1.

2.2. *Reaction Procedure*

A vacuum gasoil, whose characteristics are given in Table 2, has been cracked in a MAT unit (6) which has been designed to accomplish the ASTM D-3907 standard. It works in an automatic regime with computerized control of reactor and chromatographic analysis of gases. It is able to make a series of cyclic experiments (reaction, stripping, and regeneration of the catalyst) within a wide range of reaction conditions. Coke is measured by combustion in an air stream at 793 K for 4 h and monitoring the CO_2 formed by means of an IR cell. During the catalytic experiments, the time on stream was varied between 5, 11, 23, and 60 s. Short times on stream were always done, since it has been found that they are more adequate to describe the catalytic behaviour in a system like this, wherein the catalyst activity decays very fast (7). Experiments were carried out at different catalyst-to-oil ratios in order to obtain different conversion levels at a reaction temperature of 765 K. The reactions were performed in a fixed bed glass reactor and the catalyst was regenerated prior to each experiment.

TABLE 1

Physicochemical Characteristics of the Zeolites Used in This Work

	USY	MCM-22	ZSM-5
Si/Al	18[a]	15	31
Unit cell (nm)	2.432		
B.E.T. Surface ($m^2\ g^{-1}$)	606	414	389
μmol Pyridine adsorbed per g zeolite on Brönsted acid sites			
250°C	65	51	66
350°C	38	37	57
400°C	24	26	38
μmol Pyridine adsorbed per g zeolite on Lewis acid sites			
250°C	16	23	7
350°C	14	20	7
400°C	12	19	7

[a] Framework Si to Al ratio from DRX data; other zeolites Si to Al ratio from chemical analysis.

TABLE 2

Characteristics of Vacuum Gasoil

Density ($g\ cc^{-1}$)	0.873	Conradson Carbon (wt%)	0.03
API gravity	30.6°	MeABP (°C)	366
Nitrogen (ppm)	370	K-UOP	12.00
Sulfur	1.65	Viscosity (c.s. at 50°C)	8.249

Distillation Curve (°C)

IBP	5	10	20	30	40	50	60	70	80	90	FBP
167	245	281	304	328	345	363	380	401	425	450	551

Gases were analyzed by GC in a Varian 3400 with a two column system. Hydrogen and nitrogen were separated in a molecular sieve packed column, using argon as carrier gas and a thermal conductivity detector as the detection system. C_1 to C_6 hydrocarbons were separated in an alumina plot semicapillar column with helium as the carrier and flame ionization as the detector. Liquids were analyzed by simulated distillation.

First of all the zeolites ZSM-5 and MCM-22 were tested as cracking catalysts, together with the zeolite USY, but without previous steam treatment. All catalysts were pelletized, crushed, and sieved, a 0.59 to 0.84 mm diameter fraction was taken. Additives and USY zeolite were tested in two ways: mixed in one bed and disposed in separated beds. The quantity of zeolite plus additive was maintained at 1.60 g. When USY zeolite and additive are tested in separated beds, the first one at the top contains the USY plus silica, and the bed at the bottom contains the zeolite additive plus silica. The total quantity of zeolite plus additive plus silica was 3 g. The percentages of additive over the total catalyst was varied from 2.7 to 13.3% with the objective to clearly visualize its effect. The results were compared with the ones of the base catalyst (1.20 g of USY diluted with silica until there was 3 g of total catalyst). Then the cat/oil was calculated by dividing 3.0 g of catalyst plus silica matrix (always containing the same amount of zeolite USY, 1.20 g), by the amount of gasoil fed, which was varied in order to change the cat/oil and, therefore, to change the conversion level. In order to see the cracking behaviour after catalyst equilibration, the additive was subject to steam treatment at 1 atmosphere of steam and 1023 K for 5 h. By carrying out this steam deactivation it will be possible to determine the stability of the additive under the severe conditions present in the regenerator of the FCC unit.

3. RESULTS AND DISCUSSION

3.1. *Additive Testing Strategy*

Although pilot “riser” plants would be the logical option for deciding what cracking catalyst is more convenient according to the characteristics of the feed, economical reasons advise carrying out a first catalyst screening on the basis of the results obtained in MAT units. In this sense the actual tendency is to work each time at shorter contact times in order to be less distant from the real riser conditions (7). When testing the performance of zeolite additives, a defined strategy has not been established and generally the additive is introduced as a physical mixture, together with the main cracking catalyst.

This is done without considering how the two systems will evolve in the riser unit and how they will perform with the continuously changing "feed" along the riser reactor. However, when one takes these factors into account he may consider that in the first second of time on stream and after the catalyst has run half of the length of the riser, the large pore Y zeolite has already done most of its job and has become rapidly poisoned by coke deposition. Meanwhile, the medium pore zeolite additive, which has pores too small to convert any of the vacuum gasoil, retains most of its potential activity and starts to increasingly act when going up through the reactor, since the concentration of the accessible smaller molecules present in diesel and gasoline products will increase. In other words, the input of the zeolite additives to the product distribution will be larger in the second half of the reactor. This should be greater, if one takes into account that the rate of deactivation of ZSM-5 is much lower than that of USY zeolites (8).

Based on this we thought that the impact of a medium pore zeolite additive could be better shown by disposing the cracking catalyst and the zeolite additive in two consecutive beds in the reactor, instead of mixing the two components in a unique catalytic bed. In order to check this we have performed the cracking of gasoil on a USY zeolite catalyst, and the same catalyst with a given amount (13.3 wt% referred to zeolite Y) of ZSM-5 additive either in one uniform bed, or in two consecutive beds containing the USY on the top and the ZSM-5 at the bottom.

The results presented in Table 3, show that the effects on olefinic gases, i.e., increase in formation of propylene and butenes (including isobutene), is enhanced with the two bed disposition. On the other hand, less gasoline recracking occurs when the two zeolite beds are used, probably due to the larger stabilization of the gasoline components produced by hydrogen transfer reactions, mainly occurring in the Y zeolite, and which has to be larger when using the two bed arrangement.

Therefore, we have adopted here the two bed configuration system to study the behaviour of MCM-22 as an FCC additive.

TABLE 3

Influence of Different Disposition of Additives in the Catalytic Cracking of a Vacuum Gasoil in a MAT Reactor

Additive	Pure USY	Mixed USY + ZSM-5	Two beds USY → ZSM-5
Total conv. (%)	74.1	72.3	74.8
Gasolina (%)	39.8	30.4	33.4
Diesel (%)	13.1	11.1	11.5
Gases (%)	17.8	27.8	26.8
Coke (%)	3.4	3.0	3.1
Selectivities in the gas fraction			
$C_1 + C_2$	0.11	0.10	0.11
C_3	0.16	0.17	0.17
$C_3=$	0.16	0.18	0.20
iC_4	0.36	0.33	0.28
nC_4	0.09	0.09	0.09
Total $C_4=$	0.12	0.12	0.16
$iC_4=$	0.02	0.05	0.07

Note. Reaction conditions: Temp = 765 K, TOS = 23 s, 13.3% additive over total catalyst.

3.2. *Shape Selective Properties of MCM-22*

While catalytic test and adsorption results (5) showed that MCM-22 should have both large and medium pore channels in its structure, it was only very recently that the structure was reported (4), and we learned that MCM-22 contains two independent channel system. One is formed by 10MR channels, while the other consists of large supercages (7.1–7.1–18.2 Å) defined by 12-membered rings and interconnected by 10-membered rings. In some way one can expect this zeolite to present some of the catalytic properties of ZSM-5 zeolite, together with some selectivity features of zeolites containing large pores.

Thus we have compared the behaviour of MCM-22 and ZSM-5 when added in the same amounts to a given USY zeolite for catalytic cracking of gasoil. First of all, when used alone as the cracking catalyst (Fig. 1), it was found that MCM-22 and ZSM-5 are able to convert very little gasoil. This is an indication that the contribution of the

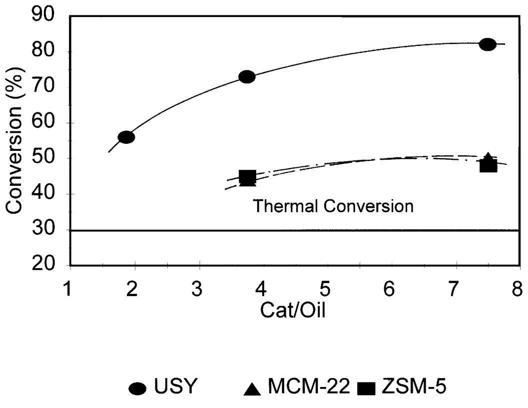


FIG. 1. Total conversion in the catalytic cracking of gasoil over (●) USY, (▲) MCM-22, (■) ZSM-5 zeolites at $T = 755$ K and TOS = 23 s.

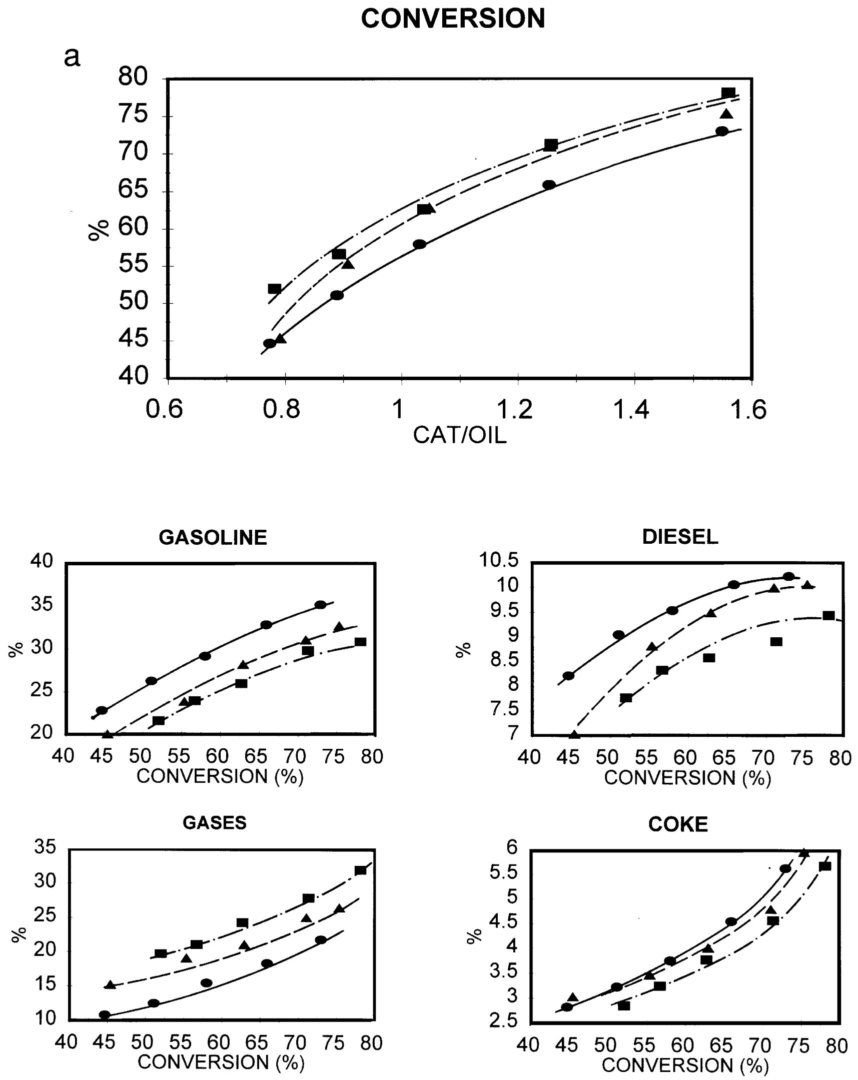


FIG. 2. Total conversion, selectivities and ratios of interest in the catalytic cracking of gasoil at $T = 793$ K, TOS = 30 s and 13.3 wt% of unsteamed additive: (●) USY, (▲) USY/MCM-22, (■) USY/ZSM-5.

large cages present on the MCM-22 to the conversion of large gasoil molecules is very limited since they are not able to diffuse through the 10-member ring windows, nor through the 10MR channels, as demonstrated by the inactivity of the ZSM-5 zeolite to crack the gasoil fraction. If this is so, in the case of MCM-22 the only cavities which may intervene in the primary cracking are those opened to the exterior, at the end of the zeolite platelets, and its effect will be a function of the thickness of the crystal platelets.

At this point and due to the low activity of the MCM-22 zeolite to crack gasoil molecules, we decide to study its possibilities when used as a FCC zeolite additive, since its channel system should be available for the paraffins, olefins, and cycloalkanes present in the distillates formed during the cracking of gasoil on the large pore zeolite Y.

3.3. Behaviour of MCM-22 as a Zeolite Cracking Additive

Fresh additive. In Fig. 2 the total conversion and selectivities are given for different catalyst to oil ratios and, therefore, for different conversion levels, at 793 K of reaction temperature and 13% of unsteamed additive over the total catalyst. The experimental data show that the MCM-22 additive yields more gasoline and diesel and less gases than ZSM-5, well in the line of the claims in Mobil patents (9, 10). The results obtained are important since one of the problems reported by using ZSM-5 as the octane additive has been a too large increase in the gases yield which may cause compressor limitations in some units. MCM-22 also yields less C_1 and C_2 gases, and this correlates well with the values of the C_3/C_4 ratio observed in the gas products. Indeed this ratio reflects the heterogeneity of the electric

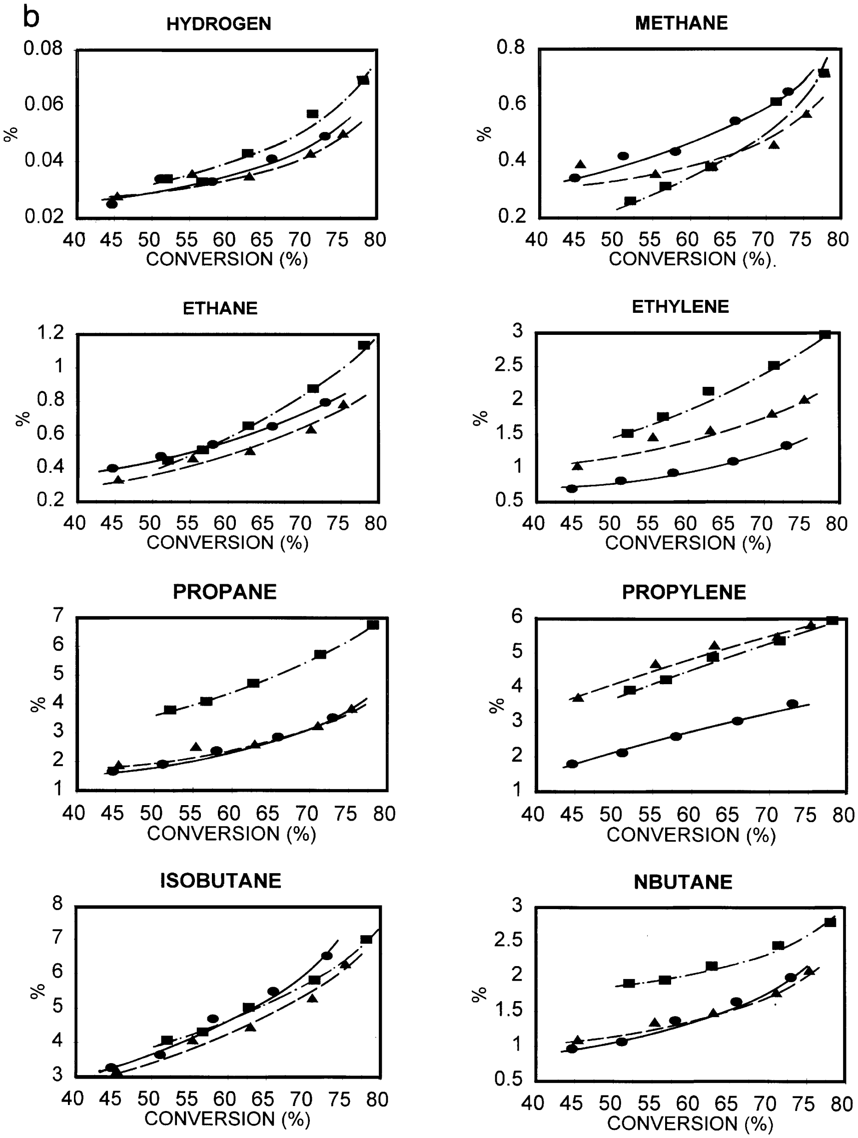


FIG. 2—*Continued*

field gradient existing in the pores of the zeolite which have a direct impact on the ratio of monomolecular (protolytic) (11) to bimolecular (β-scission) cracking mechanism (12). This concept has been used (13) to identify the presence of ZSM-5 in a FCC catalyst. When comparing with the C_3/C_4 ratio obtained with the base catalyst (USY zeolite) this ratio is higher for the additives. This indicates that on both zeolites, ZSM-5 and MCM-22, the ratio of protolytic to bimolecular mechanism is higher than for USY. Moreover, the C_3/C_4 ratio on ZSM-5 is the highest, clearly demonstrating that in the case of MCM-22 recracking occurs in both medium 10MR and 12MR channels.

The cracking mechanism ratio (CMR), which is defined as the ratio of dry gases (methane, ethane, and ethylene) to isobutane in the cracking of *n*-hexane (14) from low to high conversions, was reported to be able to distinguish between different zeolitic structures. This parameter must also be related to the ratio of monomolecular to bimolecular types of cracking, since C_1 and C_2 are typical products from protolytic cracking, while iC_4 is a typical product formed by β-scission of branched products.

We have also applied this parameter in the case of gasoil cracking to compare the behaviour of the different zeolite additives. Then, the results from Fig. 2 show that the CMR is larger for ZSM-5. This also indicates that a larger ratio of protolityc to β-scission cracking occurs on ZSM-5 than on MCM-22, in agreement with the conclusion reached from the analysis of the C_3/C_4 ratio.

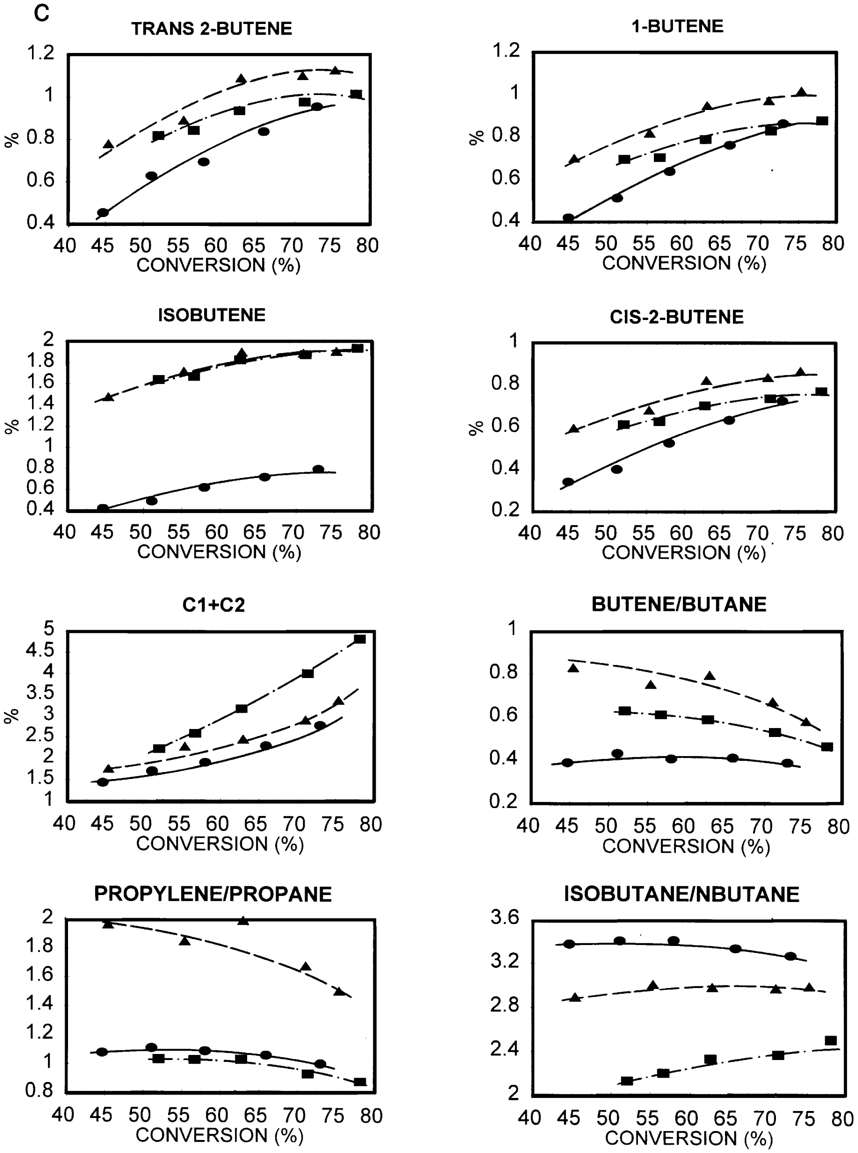


FIG. 2—*Continued*

With respect to the olefinicity of the gases it can be seen that the propylene/propane and the butene/butane ratios are higher for MCM-22. This result was surprising to us since one would expect that in the large 12-member ring cavities of MCM-22 hydrogen transfer may occur in a large extension, at least from the point of view of the space available. The fact that this was not so induces us to think that there is a relatively low amount of framework Al content in those cavities, either because originally there is a larger concentration of Al in the 10-member ring channel system, or because dealumination occurs in a larger extent in the large cavities.

We have also performed a series of experiments at 2.7% (Fig. 3) and 13.3% of additive (Fig. 4), at 755 K and 75 s of time on stream (ASTM conditions for MAT reactions). In the case of 13.3% additive, the results are similar to those obtained before at 793 K; i.e.,MCM-22 yields less total gases and dry gases than ZSM-5 and more gasoline and diesel, and their gases have a higher butene/butane and propylene/propane ratios. With 2.7 wt% of additive, the selectivities do not change qualitatively, comparing with the 13% additive, but the olefinicity ratios (butene/butane and propylene/propane) are smaller and, in any case, lower than for ZSM-5. These results indicate that at lower levels of additive ZSM-5 can be a better zeolite additive than MCM-22, but this order changes when one adds larger amounts of zeolite additive to the system.

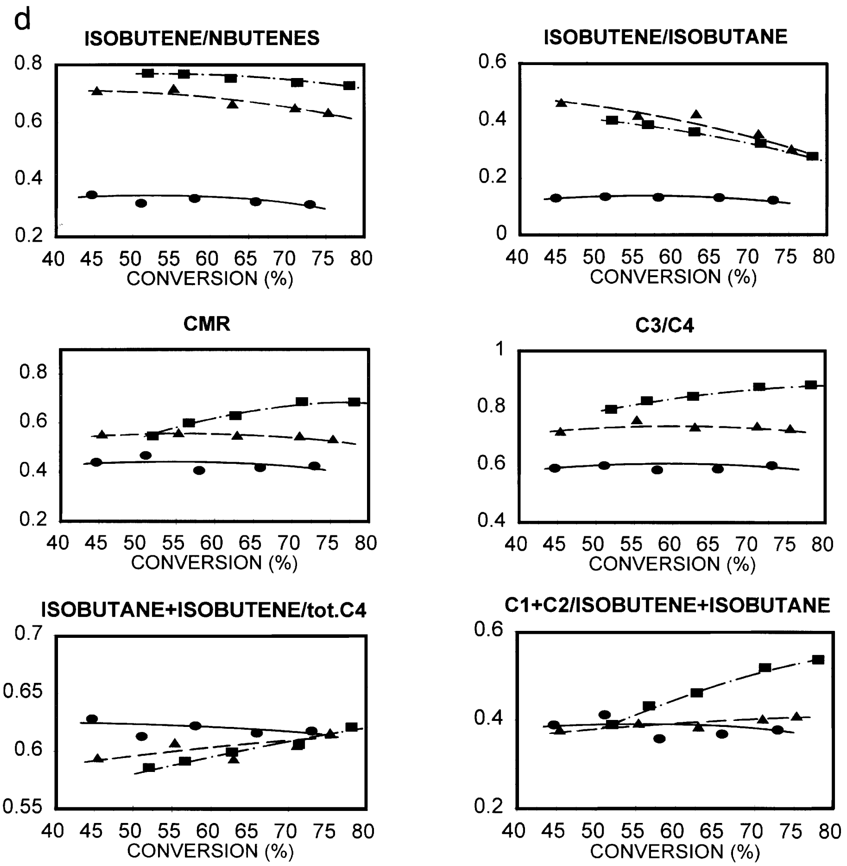


FIG. 2—*Continued*

With respect to the C_3/C_4 and the CMR ratios, both increase with the percentage of additive and either of them can be used as a yard-stick to monitor the quantity of active additive present in the reactor.

Stability of the zeolite additives. When gasoil cracking is carried out on the steamed additives, the conversion results seem to indicate that MCM-22 is even more stable hydrothermally than ZSM-5 (Fig. 5). The effects on the selectivities are qualitatively the same as the ones obtained with the fresh additives, but they are quantitatively lower due to the dealumination caused by the steaming. MCM-22 also yields more gasoline and diesel and less gases than ZSM-5. The C_3/C_4 ratio is also higher for ZSM-5 but the CMR ratio is already similar for both additives.

4. CONCLUSIONS

MCM-22 zeolite, in agreement with its structure, shows little activity when cracking a vacuum gasoil feed. This is an indication that the contribution of the large cages present in MCM-22 to cracking molecules within the gasoil fraction is very limited since they are not able to diffuse through the 10MR windows. When used as cracking additive, MCM-22 produces less total gases and less dry gases with a lower loss of gasoline than ZSM-5. Based on selectivity parameters such as the C_3/C_4 and the cracking mechanism ratio, we conclude the ratio protolytic to β-scission cracking follows the order ZSM-5 > MCM-22 > USY. The butene/butane and propylene/propane ratios are higher for MCM-22, showing adequate behaviour for reformulated gasolines. The higher olefinicity and lower protolytic to β-scission cracking ratios observed on MCM-22 with respect to ZSM-5 lead us to think that the 10MR channel system has a larger contribution to the final behaviour of MCM-22 than the 12MR cages. This may be due to the presence of an intrinsically larger concentration of framework Al in the 10MR channel system, or to the occurrence of a preferential dealumination of the cages upon zeolite activation.

However, contrary to ZSM-5, in order to see the benefits of MCM-22 as cracking additive, larger amounts (~13 wt%) need to be introduced. MCM-22 shows a good steam stability which is even higher than that of the ZSM-5 zeolite. Finally we have presented that for testing zeolite additives in MAT units, it is better to dispose the additive in a separate bed below that of the FCC catalyst, than is normally done, i.e., to physically mix both the FCC catalyst and additive in a single catalyst bed.

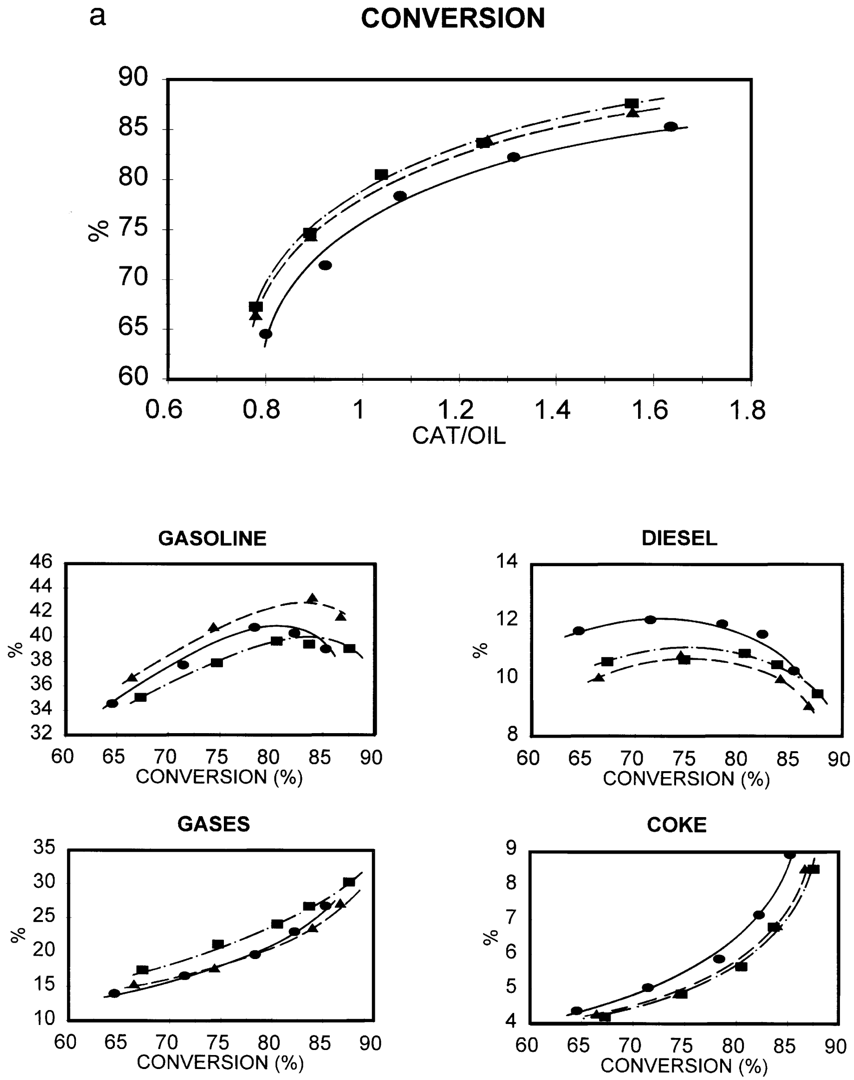
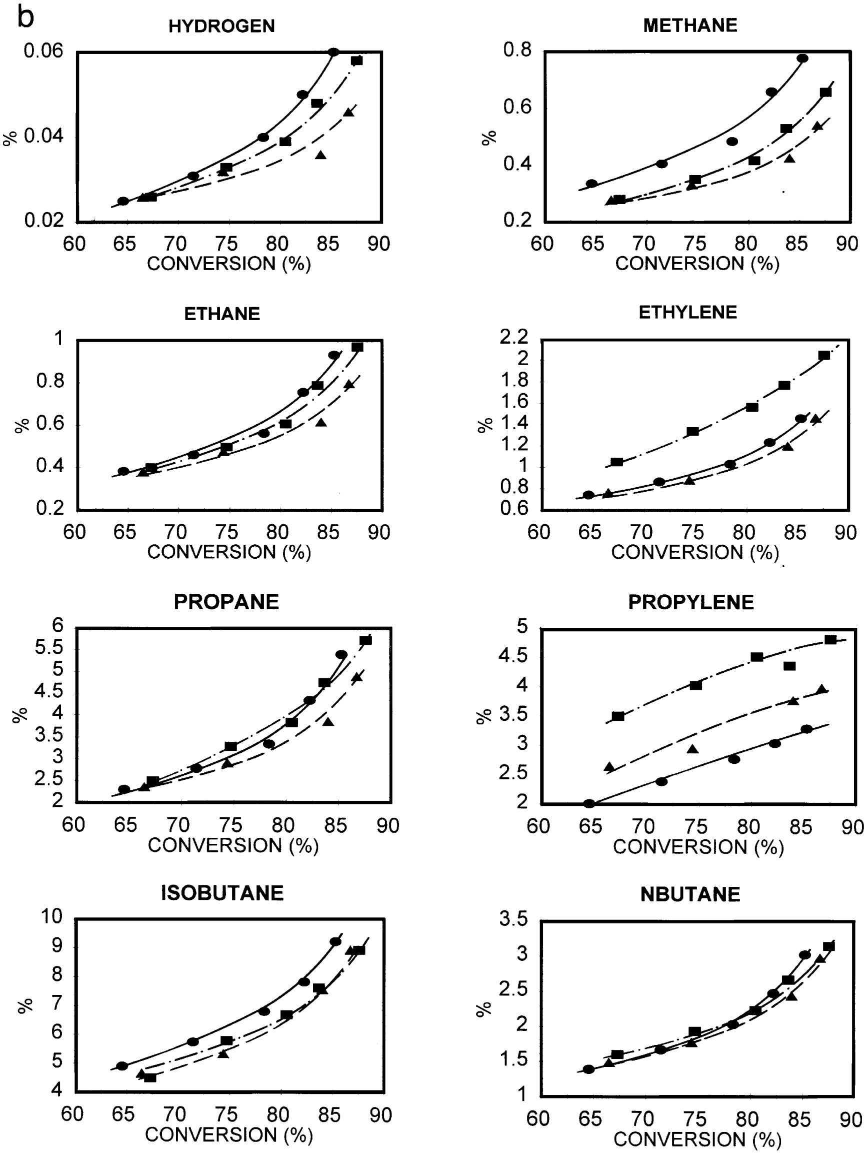


FIG. 3. Total conversion, selectivities, and ratios of interest in the catalytic cracking of gasoil at $T = 755$ K, TOS = 75 s, and 2.7 wt% of unsteamed additive: (●) USY; (▲) USY/MCM-22; (■) USY/ZSM-5.



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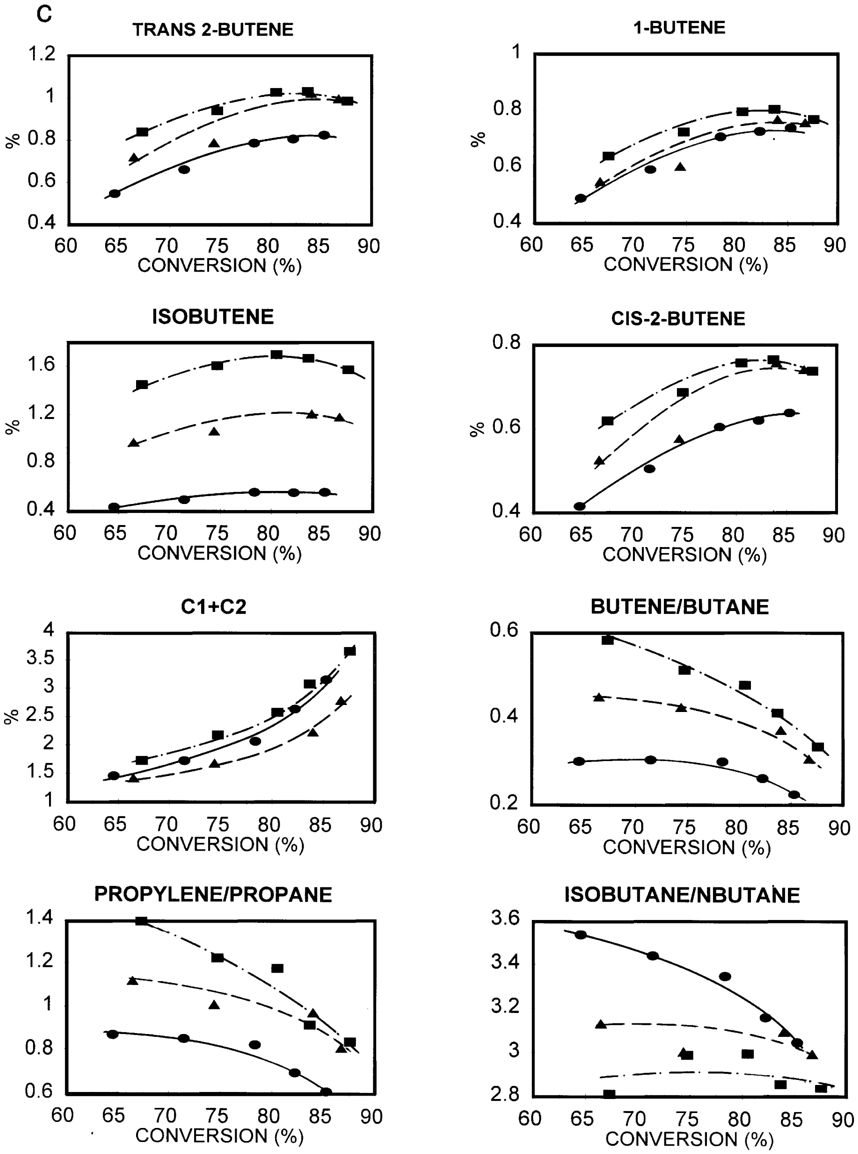

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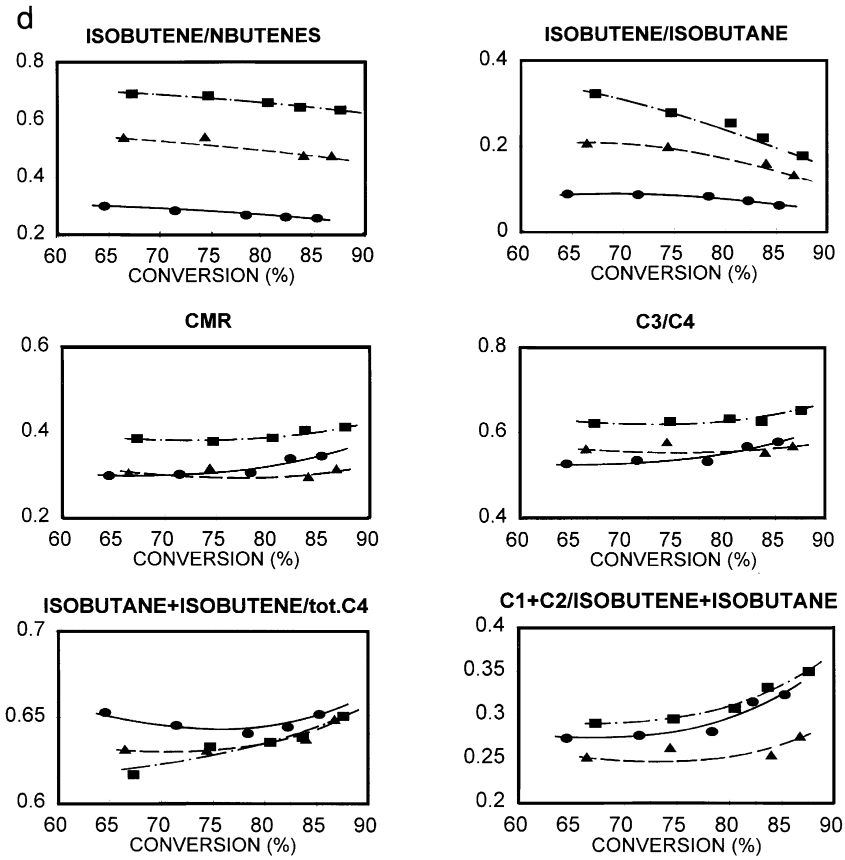

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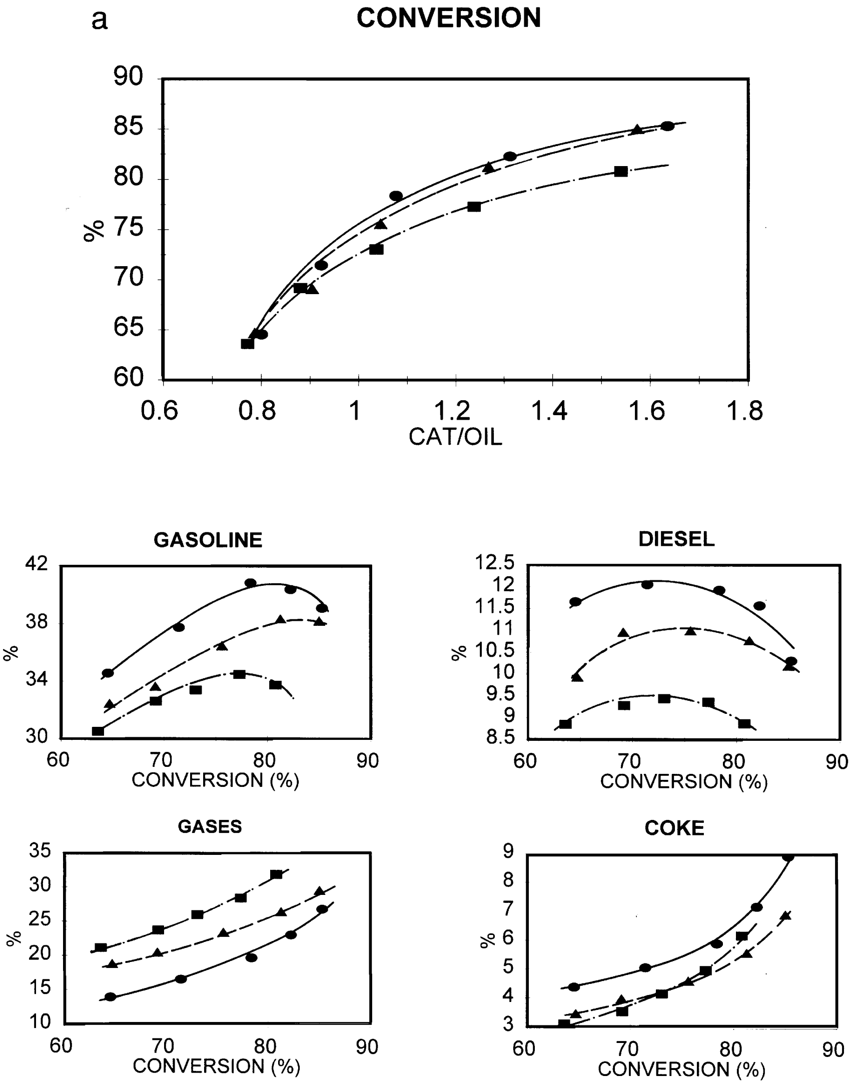
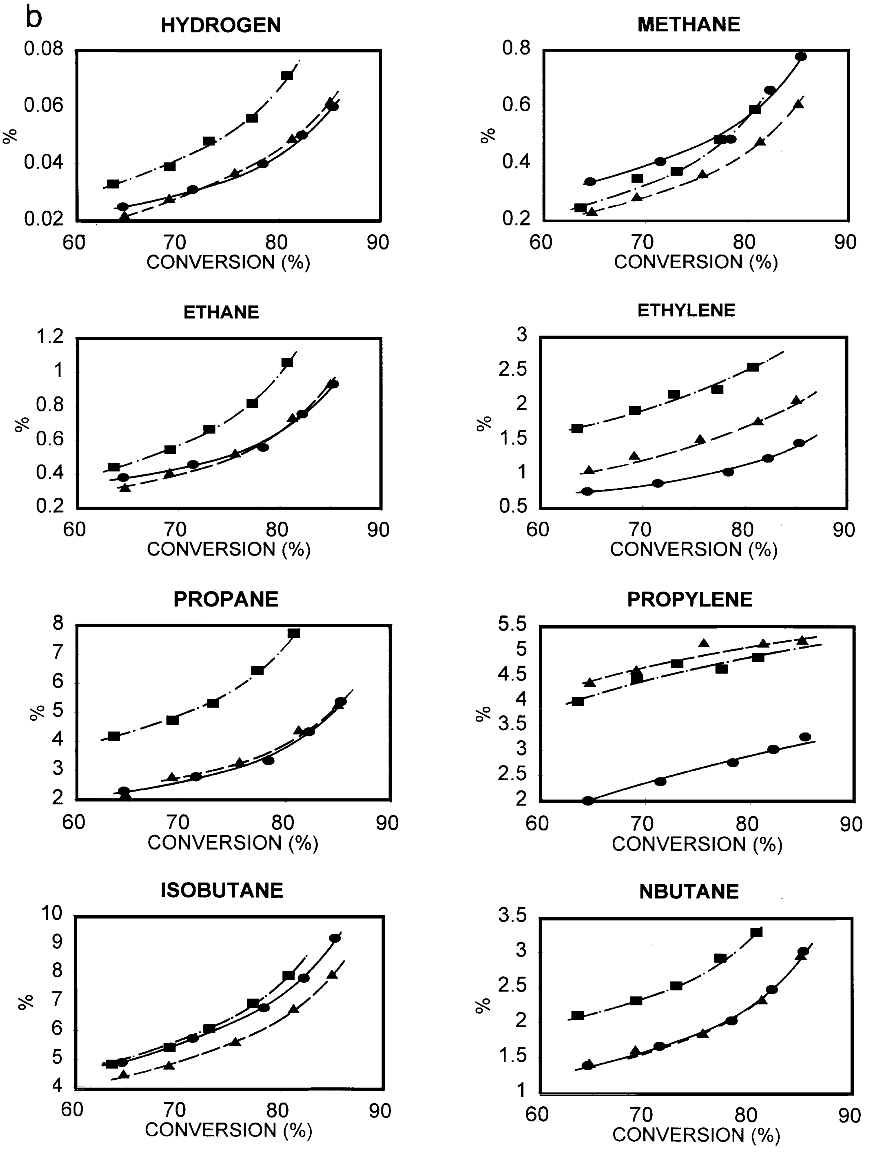


FIG. 4. Total conversion, selectivities, and ratios of interest in the catalytic cracking of gasoil at $T = 755$ K, TOS = 75 s, and 13.3 wt% of unsteamed additive: (●) USY; (▲) USY/MCM-22; (■) USY/ZSM-5.



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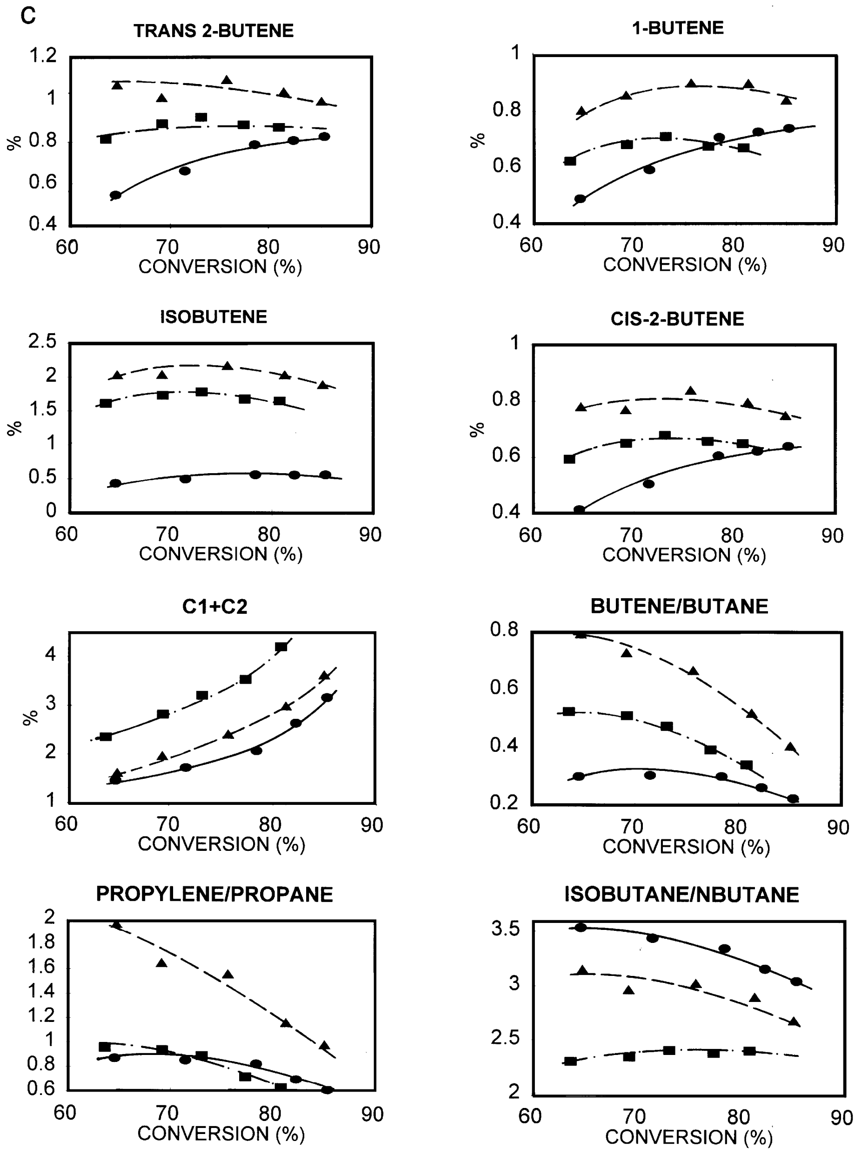

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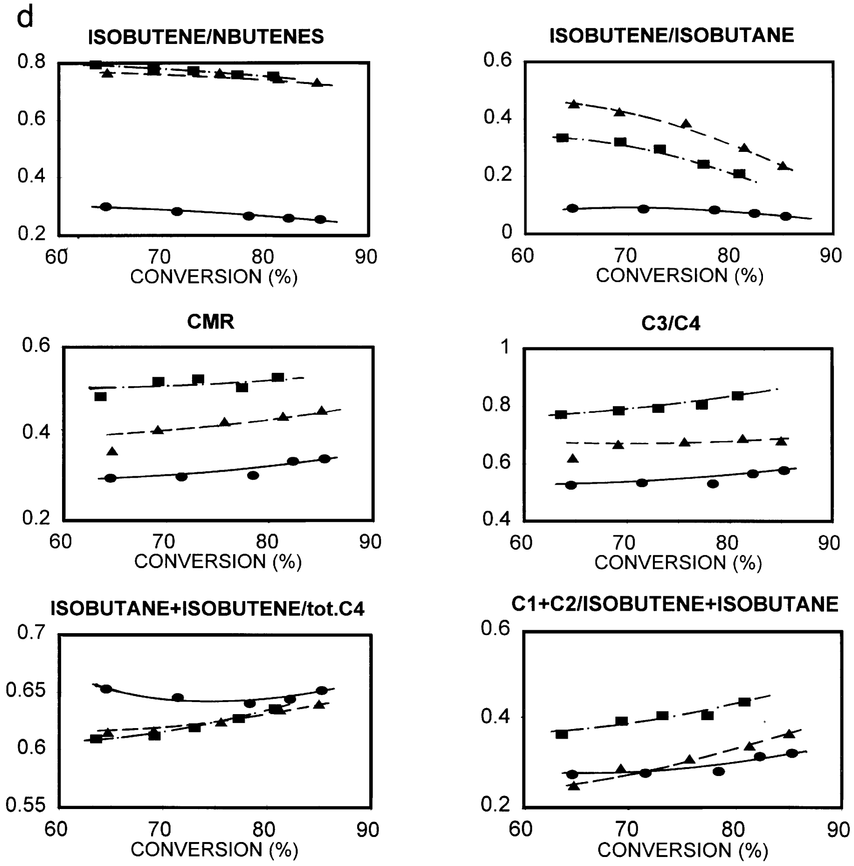

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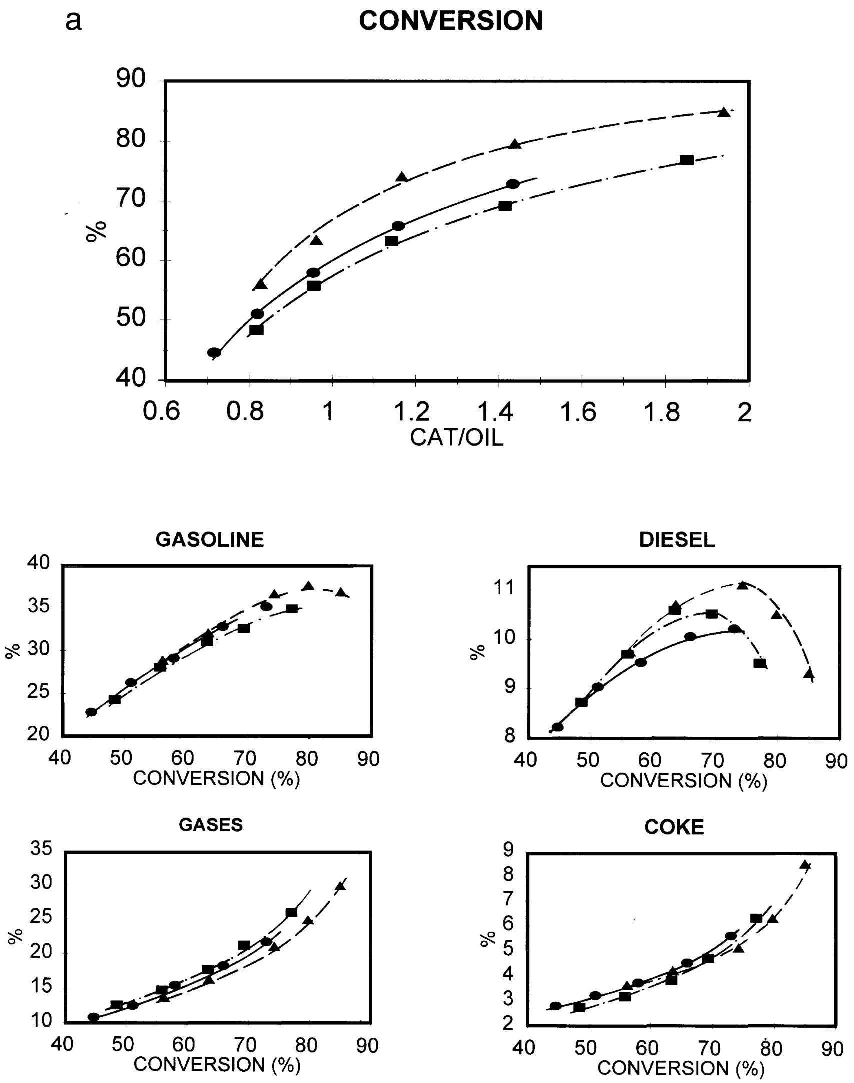
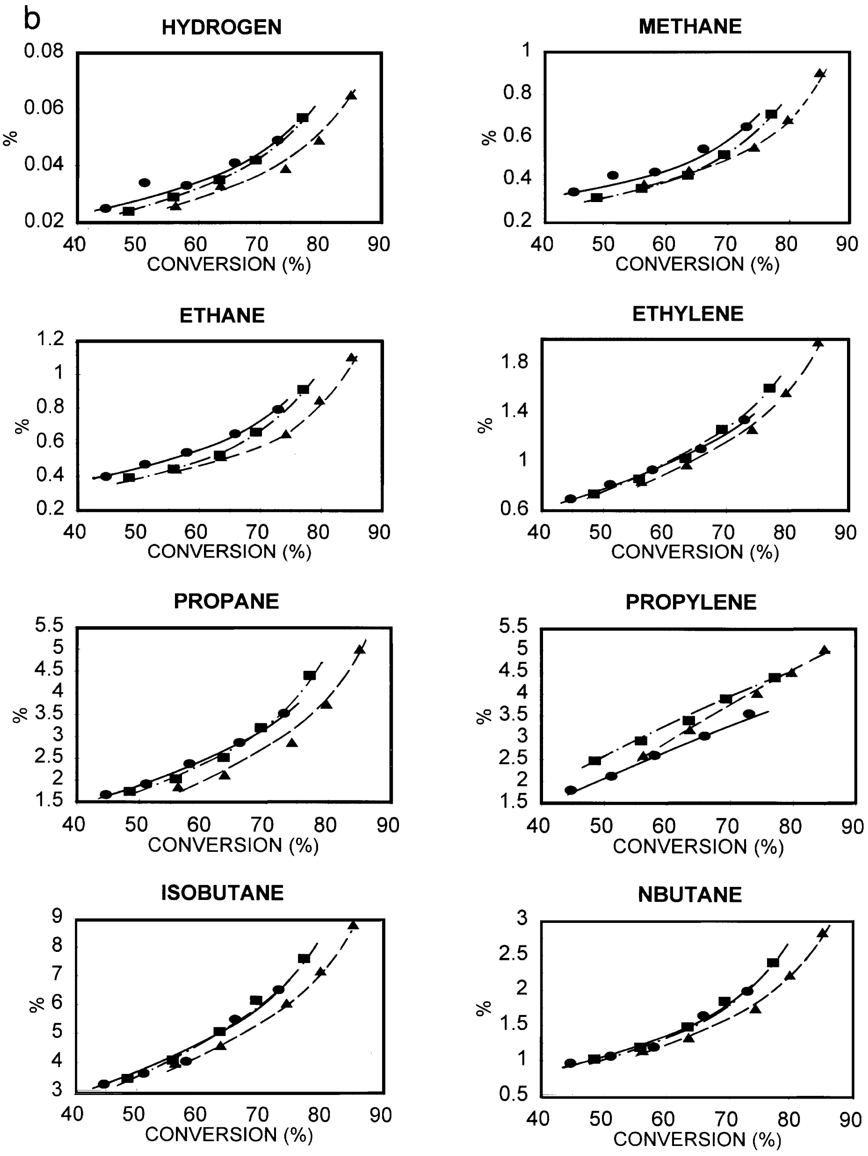


FIG. 5. Total conversion, selectivities, and ratios of interest in the catalytic cracking of gasoil at $T = 755$ K, TOS = 75 s, and 13.3 wt% of steamed additive: (●) USY; (▲) USY/MCM-22; (■) USY/ZSM-5.



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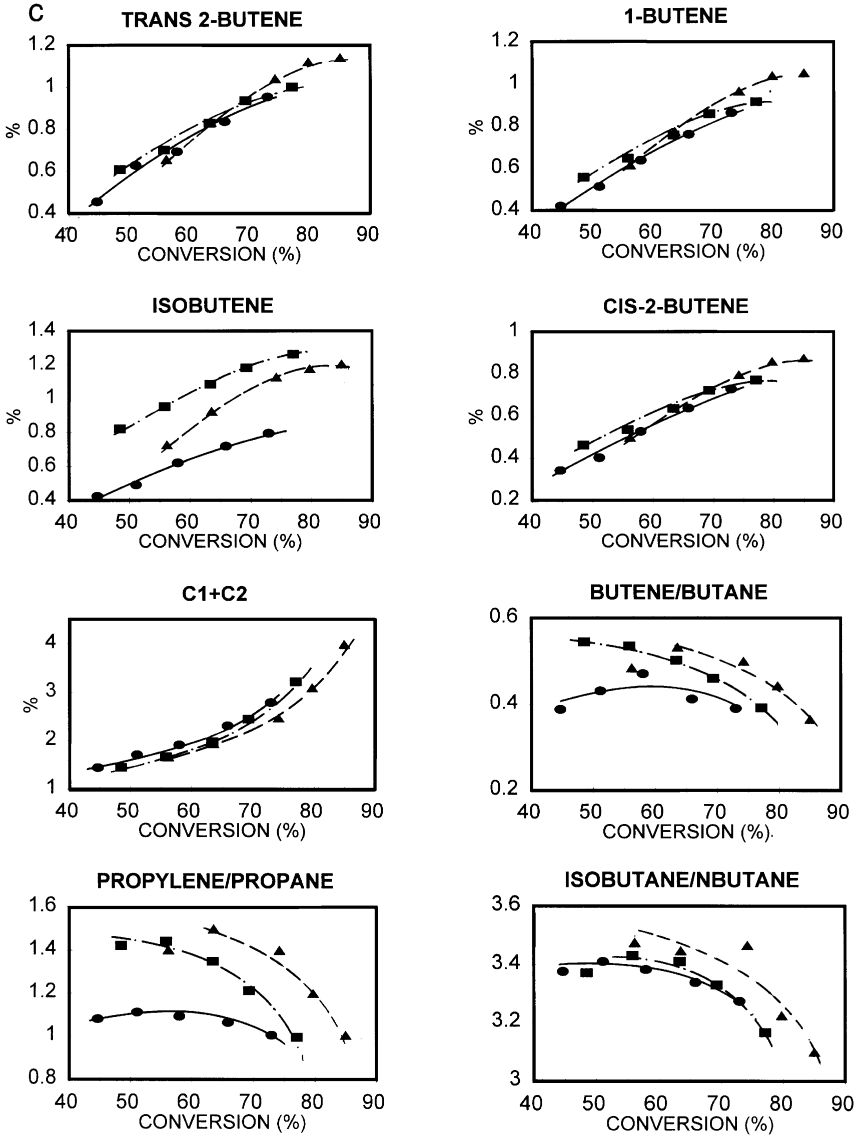

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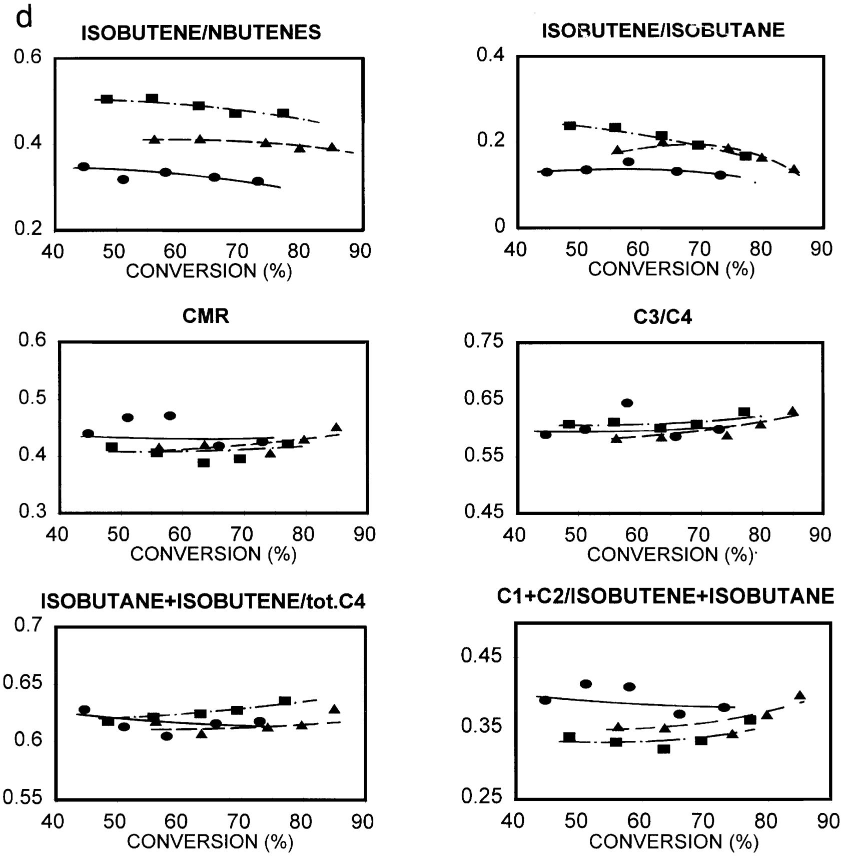

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