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Hydrogen back-spillover effects in the aromatization of ethylene on hybrid ZSM-5 catalysts

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The involvement of hydrogen back-spillover is confirmed for the aromatization of ethylene. Using hydrogen monitoring during catalytic reactions with ethylene, it has been observed that the amount of hydrogen in the gaseous effluents is much more important on hybrid catalysts than on pure ZSM-5 zeolites. The active sites on ZnO based co-catalysts are believed to be partial reduction zinc sites created during the induction period. ZnO precipitate favors the release of hydrogen species as ethane. ZnO/Al_2O_3 co-precipitate favors hydrogen recombination.

Keywords: ethylene aromatization; ZSM-5 zeolite; Zn oxide based co-catalysts; hybrid catalysts; hydrogen spillover

1. Introduction

BTX aromatic hydrocarbons (benzene, toluene, ethylbenzene, xylenes) have a high commercial value. They can be used as octane boosters in gasoline, as feedstock for plastics, as commodity chemicals, etc. Great efforts have been devoted in the last decade to finding new up-grading processes for the selective production of such monoaromatics from lower value fractions [1–5].

In the M2-forming process [1] developed by Mobil Oil, light olefins and paraffins are converted to BTX aromatics on a pure H-ZSM-5 catalyst having a SiO_2/Al_2O_3 ratio equal to 70. At the reaction temperature (538°C), cracking is important and the excess hydrogen is rejected in the form of C_1–C_3 paraffins with some molecular H_2.

Usually, in medium pore zeolites such as ZSM-5, because of sterically restricted

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environment in the channel structure and reaction loci, low hydride transfer activity is observed [6]. At low temperature, light olefins undergo rapid isomerization, oligomerization and interconversion reactions with remarkable selectivity and catalyst stability. At longer contact time or increased temperature, a shift in product distribution toward BTX aromatics and light paraffins occurs, as hydrogen transfer and cracking reactions become appreciable [6,7].

In the CYCLAR process developed jointly by BP/UOP [3], gallium is introduced by reflux in the acid ZSM-5 zeolite lattice. The resulting solid incorporates internal Ga^{3+} ions and Ga_2O_3 on the surface. It is observed that propane and *n*-butane are selectively converted to aromatics and a significant amount of hydrogen is co-produced. An additional dehydrogenation activity toward oligomeric reaction intermediates, has been attributed to gallium species formed during the reaction [8,9].

Mole et al. [10] have discussed the effects of zinc ion-exchanged in the ZSM-5. The increased selectivity for propane aromatization has been ascribed to the presence of zinc ions in the lattice, which enable the catalyst to reject hydrogen species produced during aromatization as H_2 molecules, rather than light alkanes. The rate of hydrogen out-diffusion in the zeolite channels is increased.

Hybrid catalysts are obtained by mechanically mixing the H-ZSM-5 zeolite ($Si/Al \approx 40$) with a small amount of co-catalyst (ZnO precipitate or commercial; ZnO/Al_2O_3 co-precipitate, Ga_2O_3 based oxide), both components immobilized in a bentonite clay matrix. The distance separating the two active site types has been seen to be greater than 1 μm by scanning electron microscopy. Le Van Mao et al. [11–17] have shown that hybrid catalysts can selectively convert a gaseous mixture of mainly ethylene and other light alkanes (gaseous effluent of a propane steam-cracker) or pure (paraffinic or olefinic) feedstocks, into BTX aromatics. The synergistic effect toward enhanced aromatic production, observed when a metal oxide is positioned "close" to the openings of the zeolite channels, was explained by long-distance hydrogen back-spillover (LD-HBS in acronym form). The role of the co-catalyst using the "sink" or "scavenging" actions [12a,13], is to speed up the removal of hydrogen species from the zeolite active sites where the aromatization of olefinic or paraffinic adsorbates takes place. The involvement of HBS in aromatization of light paraffins on hybrid ZSM-5 has recently been confirmed by Fujimoto et al. [18,19] using as co-catalyst alumina supported Ga_2O_3 or pure gallia and discussed by Pajonk [20].

Recent results by Le Van Mao et al. [16] have shown that α-quartz used without the addition of any metal, is also an effective co-catalyst in *n*-butane aromatization on ZSM-5 hybrids, although quartz does not chemisorb any gaseous hydrogen at the reaction temperature. The effect of α-quartz particle sizes was investigated [16]. It was demonstrated that when the average particle size of the co-catalyst is small (90 μm, BET surface area $0.7\,m^2/g$ versus 675 μm), *n*-butane conversion is increased. The aromatic yield (32.8 versus 29.1 wt% respectively) and H_2 production (0.101 versus 0.079 mol H_2/C atom respectively) are also affected. The HBS action/sink effect of the co-catalyst in the absence of metal function has been related to a decrease in surface barrier at the openings of the ZSM-5 crystallite channels, created by a second surface porosity.

The aim of this work is to define the role of the metal oxide co-catalyst in the various steps of the aromatization sequence for pure ethylene. The differences resulting from the two co-catalyst compositions (ZnO or ZnO / Al_2O_3 co-precipitate with Zn / Al ratio equal to 1.0) will be pointed out. The importance of hydrogen transfer reactions will be demonstrated.

2. Experimental

2.1. ZSM-5 ZEOLITE SYNTHESIS

A ZSM-5 zeolite having a Si/Al atomic ratio of 43 was synthesized according to the method of Argauer and Landolt [21]. The procedure to obtain the acid form, also called H-ZSM-5, by repeated ion-exchange with NH_4Cl and then calcination at 550°C, as well as characterization techniques used on the synthesis product and the zeolite powder in its acid form are as described in previous references [11–17]. Table 1 reports the results of characterization experiments.

Prior to using a new zeolite, standard catalytic tests for pure and hybrid catalysts were conducted to ensure uniformity and reproducibility with previously synthesized batches.

Table 1
Physico-chemical properties of the various hybrid catalyst components

Zeolite [a]	Si/Al ratio	Na_2O (wt%)	DC [b]	BET surface area (m^2/g)	Total acid density [c] ($\times 10^4$ mol/g)
H-ZSM-5	43.0	0.10	99.5	390	4.8

Co-catalyst [d]	Zn/Al ratio	BET surface area (m^2/g)	Average pore size (Å)
(treated at 550°C for 12 h)			
ZnO precipitate	∞	3.6	70
ZnO / Al_2O_3 co-precipitate	1.0	27.4	98
Matrix			
bentonite clay (extrudate)	–	2.3	169

[a] Zeolite average particle size (SEM) 2–3 μm.
[b] Degree of crystallinity determined by XRD (%).
[c] Total acid density measured by NH_3-TPD.

2.2. SYNTHESIS OF THE CO-CATALYSTS

The co-catalysts were synthesized by heterogeneous co-precipitation according to the preparation method described in previous work [11]. Only pure ZnO and a co-precipitate of ZnO/alumina (from aluminium sulphate salt) having a Zn/Al ratio equal to 1.0 were used. The co-catalysts were crushed and sieved (80–100 mesh). The oxide powders were characterized by atomic absorption, X-ray powder diffraction, BET surface area, scanning electron microscopy (SEM), hydrogen chemisorption and TPD of ammonia (table 1).

2.3. HYDROGEN CHEMISORPTION MEASUREMENT

To measure the hydrogen adsorption capacity of the co-catalyst powders, extrudates (0.8 g) were loaded in a quartz reactor and pretreated at 550°C under flowing He overnight. Using a volumetrically calibrated loop (1 ml), hydrogen gas was pulsed at 500°C. The effluent was monitored using a SRI student GC equipped with a thermal conductivity detector (TCD) and set on-line with the system. The amount of nonadsorbed hydrogen gas was estimated by integration of the chromatographic trace obtained for every pulse. Known amounts of H_2 were injected into the GC as a volumetric calibration procedure, so the TCD responses could be reported as moles H_2/ pulse. The differential between total moles H_2 pulsed and the recorded nonadsorbed fraction indicated the capacity for adsorption of the co-catalyst surface at 500°C, a temperature used in the catalytic reactions.

2.4. PREPARATION OF THE CATALYSTS

To prepare the final catalysts, the H-ZSM-5 powders (mesh size higher than 60) and zinc oxide–aluminium oxide or zinc oxide precipitate powders (mesh size higher than 60) were mechanically mixed at room temperature. The required amounts varied between 0 and 80 wt%. Bentonite clay (20 wt%) was then incorporated and intimately mixed with the solid catalyst. Deionized water was added dropwise until a malleable paste was obtained. The latter was extruded into 1.5 mm o.d. *spaghettis*. The final extrudates were dried at 120°C overnight and activated in air at 550°C for about 10 h. The final length of the catalyst extrudates was 5 ± 0.5 mm.

To prepare the samples where the co-catalyst was introduced by a dry impregnation technique, instead of using deionized water to obtain a malleable paste, an aqueous solution containing the required amount of zinc nitrate and/or aluminium sulphate were used. The principle of this incorporation method [12a] is that: as the aqueous solution is added, it is preferentially absorbed by the bentonite clay which acts as a sponge. Upon extrusion, the force causes the zinc or aluminium hydroxyls to migrate onto the exterior of the zeolite particles, precluding their impregnation inside the zeolite lattice. In the activation step conducted at 550°C, the oxides are formed on the surface of the zeolite particles and a situation of intimacy exists between the zeolitic and oxide components.

2.5. CATALYTIC TESTING

Catalytic testing and the experimental set-up used were described elsewhere [11]. The feed was pure ethylene in nitrogen (carrier gas, 20 ml/min). The usual reaction parameters were as follows: temperature R_c: 500 ± 0.5°C; WHSV (weight hourly space velocity: weight feed ($g\,h^{-1}$)/ weight catalyst (g) = $0.6\,h^{-1}$; weight catalyst: 4 g; duration of a run: 4 h.

For experiments where the catalyst was reduced prior to the reaction, a mixture of H_2 in N_2 was used with the catalytic reactor heated at 400°C for 3.5 h.

For experiments where H_2 was co-fed, the carrier gas/hydrogen mixtures in required amounts were mixed prior to contact with the hydrocarbon feed.

The liquid hydrocarbons produced were collected in condensing flasks kept at −15°C. The gases were analyzed throughout the run using a Shimadzu GC (model Mini 3, FID) equipped with a 2.5 m stainless steel column (15 wt% squalane on Chromosorb P) with 2,2-dimethylbutane as internal standard. The amount of hydrogen in the effluent was measured chromatographically using a 30 m Haye-Sep DB column from Chromatographic Specialties (HP model 5890-TCD/N_2 carrier gas). Prior to analysis, a volumetric calibration was performed using pure hydrogen gas. The collected liquid phases were subsequently analyzed with a Hewlett Packard GC (model 5790A, FID) equipped with a 50 m PONA type capillary column. When required, *n*-octane was used to extract the organic phase prior to chromatographic analysis. The *n*-octane peak was considered as solvent in the chromatogram and excluded from the product distribution.

2.6. PRODUCT CALCULATIONS

All calculations were made on a carbon atom basis. Chromatographic results were converted to C atoms using an internal standard (2,2-dimethylbutane) for the gaseous effluent and correction factors for the columns.

In the following data, the total conversion of feed is defined as

$$C_t(\text{C atom\%}) = \{[(\text{NC})_F - (\text{NC})_P]/(\text{NC})_F\} \times 100 = \{(\text{NC})_R/(\text{NC})_F\} \times 100\,,$$

where $(\text{NC})_F$, $(\text{NC})_P$ and $(\text{NC})_R$ stand for the number of C atoms of hydrocarbon source fed to the reactor, the gaseous effluent and reacted, respectively.

The selectivity for product *i* is defined as

$$S_i(\text{C atom\%}) = \{(\text{NC})_i/(\text{NC})_R\} \times 100\,,$$

where $(\text{NC})_i$ is the number of C atoms of product *i* in the outstream gases.

The yield for product *i* is defined as

$$Y_i(\text{C atom\%}) = S_i C_t \times 1/100\,.$$

It is worth noting that bentonite used as a binder does not show any significant catalytic activity [11a,14].

3. Results and discussion

Monitoring the amounts of molecular hydrogen in the outstream gases during reactions has provided direct evidence for the involvement of the co-catalyst in hydrogen removal during ethylene aromatization. Table 2 reports the obtained values for pure and hybrid catalysts of ZnO or ZnO/alumina co-precipitate (Zn/Al = 1.0), where the amounts of co-catalyst were 5 wt%. Column A shows typical product selectivities for pure H-ZSM-5, with associated total hydrogen production and rate of hydrogen production normalized in time. Columns B and D show product selectivities and hydrogen productions for fresh hybrids of ZnO/Al_2O_3 co-precipitate and ZnO respectively. Results of columns C and E represent catalysts B and D respectively, reduced prior to reactions in 30% H_2/N_2 mixtures for 3.5 h at 400°C.

From table 2, it can be seen that within experimental error (2–3%), ethylene conversions are constant for all catalysts. Constant ethylene conversions form a common baseline and allow us to ascribe the differences in selectivity to the variations in chemical composition or pretreatment of the catalysts.

Table 2
Aromatization activity and corresponding H_2 evolution on pure and hybrid catalysts (catalysts A–E, see text). Effect of reduction on catalytic activity of the hybrids

	Total product selectivity (% C atoms)				
	A	B	C	D	E
C_1–C_4 paraffins	39.5	26.3	20.3	40.0	37.0
(ethane)	(4.3)	(16.5)	(8.9)	(33.4)	(29.0)
C_3–C_4 olefins	18.4	6.4	8.8	4.6	3.4
C_{5+} aliphatics [a]	6.8	1.9	2.5	1.0	0.9
total aromatics	35.4	65.4	67.9	54.4	58.7
BTX/aromatics	0.83	0.86	0.85	0.83	0.79
ethylene conversion (% C atoms)	92.3	92.2	91.1	89.0	93.7
total H_2 produced (mmol)	5.4	29.5	44.6	19.8	26.4
rate H_2 production (mmol/h)	5.8	30.5	31.1	16.2	18.9
H_2/aromatics (molar ratio)	0.4	1.3	1.7	1.2	1.0

[a] C_{5+} aliphatics: aliphatic molecules having 5–10 C atoms.

Upon comparison of A versus B, D, it can be observed that the addition of a co-catalyst surface favors the out migration of hydrogen species (30.5 and 16.2 mmol H_2/h versus 5.8 mmol H_2/h). The jump in H_2 production is paralleled by increased conversions of C_3–C_4 olefins and C_{5+} aliphatics to total aromatics. Removal of hydrogen adspecies from the zeolite's internal acid sites results in higher efficiency of the lattice for aromatization. Enhancements of 46 and 35% respectively for B and D hybrids versus the pure ZSM-5 parent are obtained under identical reaction conditions.

Upon comparison of ethane selectivities and the rates of H_2 production recorded for hybrids of mixed oxides and pure oxide co-catalysts (B versus D), it is found that:

(1) The sink action [12a,13] resulting in lower ethane production and higher $H_{2(g)}$ release by recombination is predominant on ZnO/Al_2O_3 co-precipitate (fig. 1).

(2) The scavenging action resulting in lower hydrogen production and higher ethane formation predominates on ZnO. The net effect of the scavenging action is the loss of potentially aromatizable ethylene by a side reaction on the co-catalyst surface.

Reduced catalysts in columns C and D show the same trends as their fresh analog, however H_2 productions are increased. For a fresh or oxidatively regenerated hybrid an induction period characterized by low $H_{2(g)}$ and ethane fractions in the gaseous effluent is observed, and the "steady-state", achieved by a constant product distribution, is only attained 40–50 min after the start of the reaction. Since

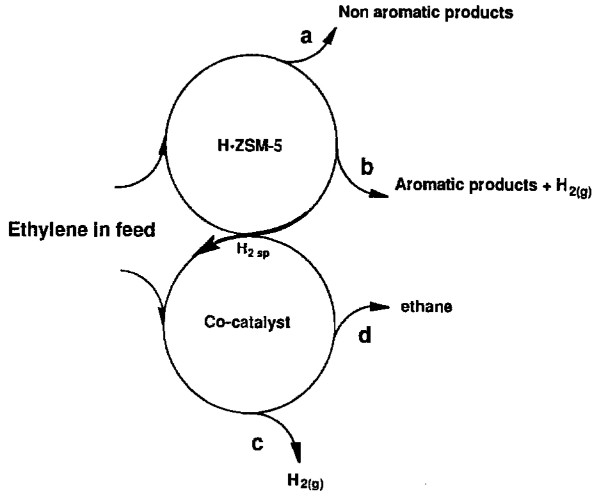

Fig. 1. Proposed catalytic cycle on hybrid catalyst: feed = ethylene. (a) Oligomerization products, (b) cyclization/ dehydrogenation products, (c) sink effect of co-catalyst/desorption of $H_{2(g)}$, (d) scavenging effect of co-catalyst/reduction of ethylene. H_{2sp}, spiltover hydrogen species/surface migration across particle boundaries.

hydrogen gas pretreatment submits the catalysts to a reductive atmosphere prior to reaction, it is believed that changes on ZnO or ZnO/alumina co-precipitate are similar to the modifications caused by migrating hydrogen species during the induction period.

ZnO acid–base pairs are known to chemisorb H_2 by heterolytic cleavage [22]. As a result, ZnO is reduced and a Zn(0) defect site created in the lattice. ZnO, a typical n-semiconductor, also looses some of its lattice oxygens upon thermal treatment (around 500°C) [23]. Non-stoichiometric excess of zinc as Zn(I) and Zn(0) are produced on the surface, associated with localized electron excess concentrations. These defect sites could be the active sites responsible for dissociative adsorption of spiltover hydrogen species exiting the zeolite channels. This conclusion was also put forth by Spinicci and Tofanari [23] using ESR spectroscopy correlations of ZnO based catalysts in studies of propylene dehydroaromatization.

The presence of alumina in the co-precipitate helps to free the Zn–O active sites from adspecies by promoting molecular hydrogen desorption (enhanced sink effect on ZnO/Al_2O_3) [24]. IR spectroscopic studies [25] have shown that hydrogen can dissociatively adsorb on η- and γ-alumina. Temperature programmed desorption studies [26] have shown that on alumina-supported metals, dissociatively adsorbed hydrogen is able to spillover until the surface is equilibrated. The reactivity of spiltover hydrogen species toward hydrogenation of unsaturated molecules on alumina has been demonstrated to be very low [27–29], therefore inhibiting the reduction of potentially aromatizable ethylene.

Fig. 2 depicts the results of hydrogen chemisorption studies conducted at 500°C on fresh ZnO and ZnO/Al_2O_3 co-precipitate (Zn/Al = 1.0) samples. It can be seen that the adsorption capacity of fresh ZnO/alumina is smaller than that of zinc oxide. Table 3 shows that if hydrogen adsorption capacity is reported per unit surface area, ZnO possesses twice the capacity of ZnO/Al_2O_3. Since the co-precipi-

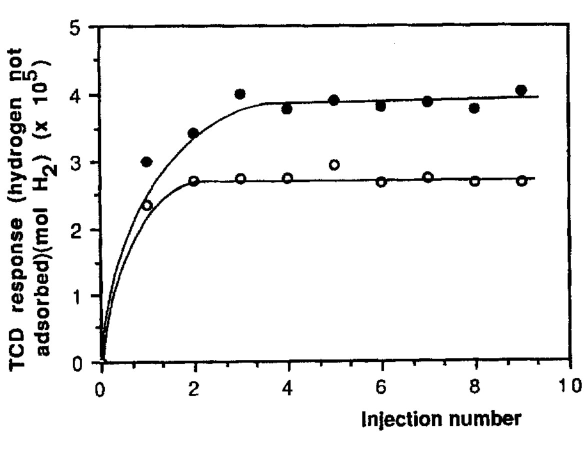

Fig. 2. Hydrogen chemisorption studies of co-catalysts performed at 500°C. (●) ZnO hybrid, (○) ZnO/Al_2O_3 hybrid (Zn/Al-S = 1.0).

Table 3
Results of hydrogen chemisorption experiments for the co-catalysts performed at 500°C

	Catalyst	
	ZnO precipitate	ZnO/Al_2O_3 co-precipitate (Zn/Al = 1.0)
hydrogen adsorption capacity per unit weight (mol/g)	4.249×10^{-5}	16.02×10^{-5}
hydrogen adsorption capacity per unit surface area (mol/m_2)	1.180×10^{-5}	0.5857×10^{-5}

tate has a Zn/Al atomic ratio equal to 1.0 or 50 mol% Zn in its chemical composition, it follows that only active sites on ZnO can directly adsorb H_2 from the gas phase. However, it has been seen that (table 2) ZnO/Al_2O_3 co-precipitate has a higher efficiency for hydrogen release than pure ZnO after the initial induction period. It is believed that alumina becomes activated during the reaction by spiltover hydrogen species and promotes the hydrogen recombination. It then behaves as a third component promoting hydrogen recombination. The importance of the configuration of the (chemi)sorption sites of the metal species was also recently observed with the Ga hybrid catalysts [17].

Due to the importance of hydrogen in the explanation of enhanced aromatic selectivity, the effect of hydrogen partial pressure was systematically studied in ethylene aromatization. The catalysts compared were: pure H-ZSM-5, ZnO/Al_2O_3 co-precipitate (Zn/Al = 1.0) and ZnO precipitate hybrids.

The effects of increasing hydrogen partial pressures on the parent zeolite are depicted in figs. 3A (aromatic yields), 3B (ethane yields) and 3C (H_2 production). It can be observed that the progressive addition of $H_2(g)$ slowly shifts the reaction mechanism to a new pathway, reflected in a slow drop in aromatic formation.

Comparing figs. 3A, 3B, 3C for both hybrid catalysts, sharp decreases in aromatic yields and hydrogen productions can be observed, reflecting the inability of the co-catalyst surfaces to keep up as effective hydrogen adsorbents (for spiltover hydrogen species). In effect, the addition of hydrogen gas acts as a poison, blocking the available sites to adspecies exiting the zeolite channels. The decreasing aromatic yields are counterbalanced by increased formation of ethane. Particularly for the ZnO hybrid, although the co-catalyst accounts for only 5 wt% of the total chemical composition, a clear shift from aromatization to hydrogenation reaction is seen with increasing hydrogen partial pressures. The ethane production on the co-catalyst uses the hydrogen gas supplied with the feed and ethylene adsorption by the internal zeolite acid sites is almost completely suppressed.

Severe "poisoning" effects of added hydrogen partial pressure on catalytic activity and selectivity of hybrid systems, clearly demonstrate the involvement of HBS in explaining enhanced aromatic production.

Fig. 4 shows SEM photographs of configurational arrangement in fresh and

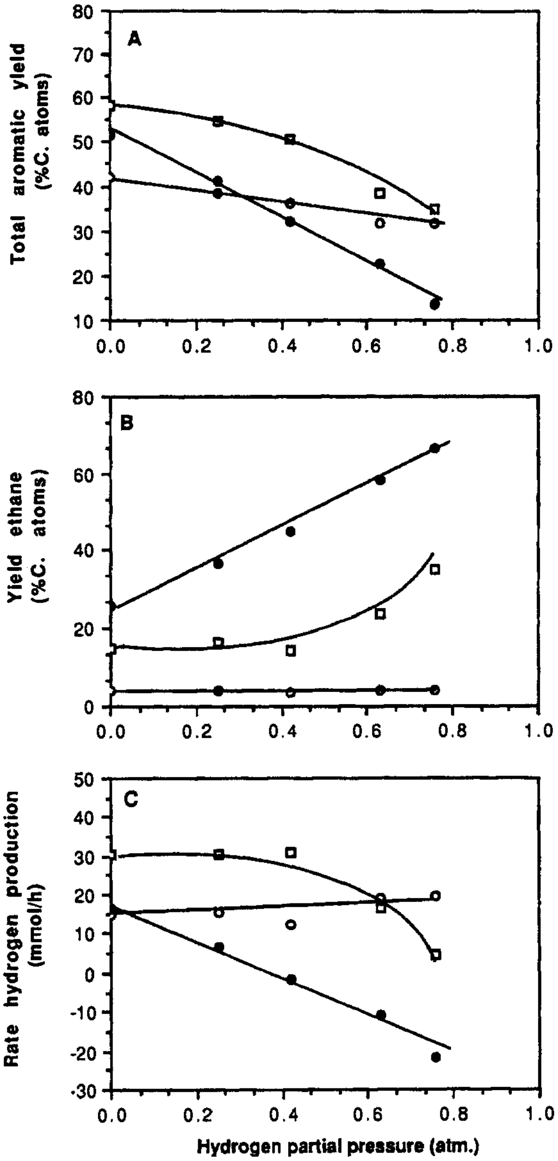

Fig. 3. Effect of added feed hydrogen on catalytic activity of pure and hybrid catalysts in the aromatization of ethylene. Catalyst composition: (pure) 80 wt% H-ZSM-5 + 20 wt% bentonite binder, (hybrids) 75 wt% H-ZSM-5 + 5 wt% ZnO/Al_2O_3; (Zn/Al = 1.0) co-precipitate or ZnO + 20 wt% bentonite binder. (○) H-ZSM-5, (●) ZnO hybrid, (□) ZnO/Al_2O_3 hybrid.

used ZnO/Al_2O_3 co-precipitate (Zn/Al = 1.0) hybrid systems, in order to show the arrangement of particles.

On the fresh sample (A), the different dimensions of zeolite and sieved co-catalyst particles can be observed (2–3 μm versus ≈ 80 μm). Since the co-catalyst accounts for a much smaller weight percentage of the catalyst composition, the particles are

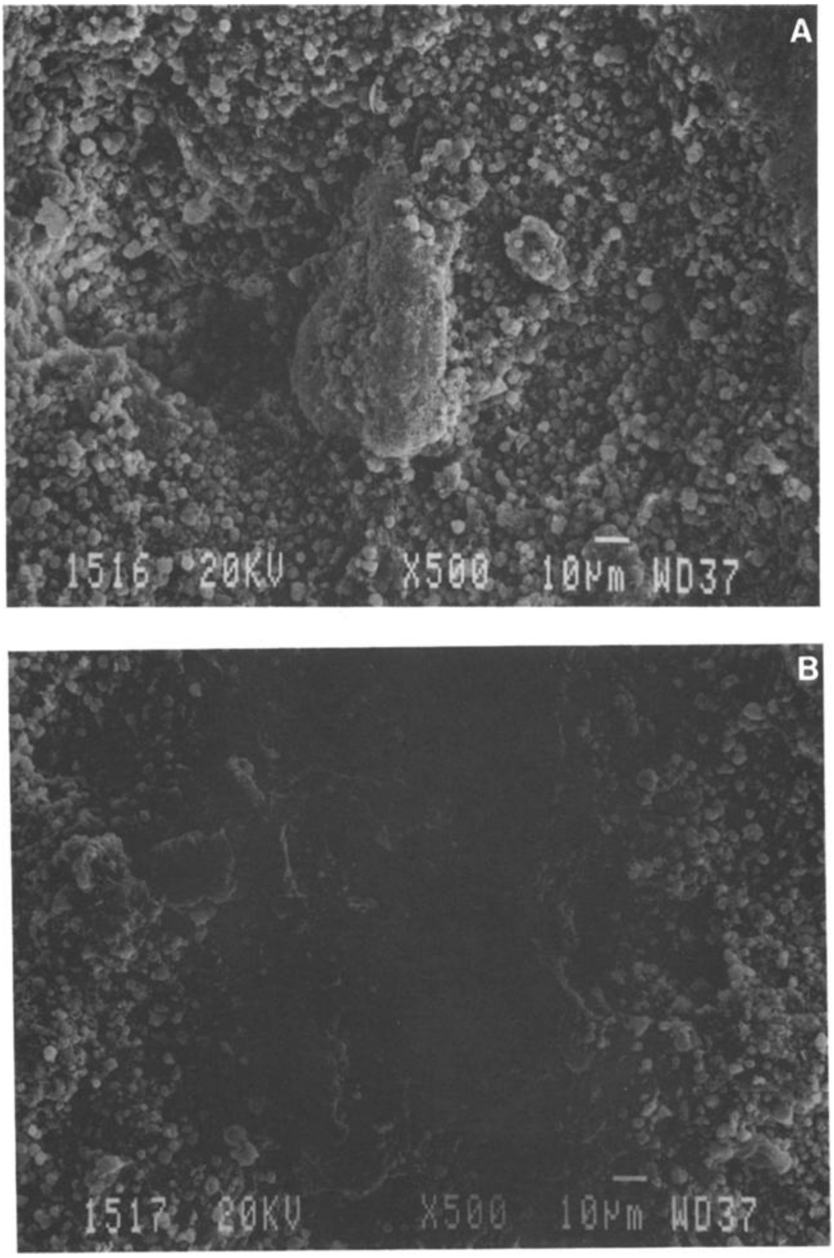

Fig. 4. SEM photographs of hybrid catalyst in the extrudate form. (A) Fresh ZnO/Al_2O_3 co-precipitate ($Zn/Al = 1.0$) hybrid, (B) used ZnO/Al_2O_3 co-precipitate ($Zn/Al = 1.0$) hybrid.

not homogeneously distributed, and the majority of zeolite particles do not share an interface with the co-catalyst. Since the global performance of the zeolite is modified by addition of a small amount of co-catalyst, the effects operate on large distances.

On the used sample (B), it can be observed that the co-precipitate particle is broken compared to its fresh analog, and the zeolite particles are more intimately mixed since partial reduction of the lattice occurs. Upon adsorption of dissociated hydrogen species, and since Zn^0 becomes volatile around 500°C (reaction temperature), removal of some metallic zinc atoms is believed to be involved in co-catalyst structure collapse with concurrent rearrangement of zeolite particles. EDAX (energy dispersive X-ray) chemical analysis of the peripheral environment did not indicate migration of zinc to the zeolite framework.

Partial reduction of the co-catalyst is seen as prerequisite for efficient removal of hydrogen adspecies from the zeolite channels (also seen in table 2). The creation of surface defect sites such as: partially reduced zinc (Zn^+) [22] or oxygen vacancies are believed to be the adsorption sites for spiltover hydrogen species and co-adsorbed ethylene.

4. Conclusions

In this work, the importance of hydrogen transfer activity within the zeolite lattice was demonstrated. Produced hydrogen species during the dehydrocyclization step of the reaction depressed the aromatic yield as a result of active site occupation. Evacuation of hydrogen in the form of spiltover species (most likely dissociated H_{2sp} in fig. 1) was promoted by admixing another surface at the exit of the zeolite channels. Severe poisoning by hydrogen partial pressure on hybrids was taken as clear evidence for the involvement of HBS.

The actions of ZnO and ZnO/alumina (Zn/Al = 1.0) co-catalysts were scrutinized. ZnO was established as a promoter of ethylene reduction into ethane (scavenging). Zn–O pairs were confirmed as initial adsorbents for spiltover hydrogen species in chemisorption studies. Partially reduced Zn–O acid–base pairs were postulated as active sites on the ZnO surface. The activated alumina surface of the ZnO/Al_2O_3 co-precipitate was used to explain the increased hydrogen evolution in the gaseous effluent (sink).

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