

Effect Of Hydrogen Reduction On Catalytic Activity Of Cr-ZSM-5 In The Decomposition Of Ethyl Acetate And Benzene In Air

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ABSTRACT

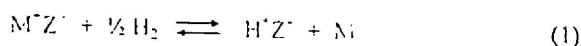
The physical and chemical changes occurred after hydrogen reduction treatment on chromium exchanged ZSM-5 (Cr-ZSM-5) and the effect of these changes on the catalyst's activity are reported. Ethyl acetate and benzene were selected as air-borne VOC pollutant model compounds. Catalyst reduction was performed under 100 ml/min of pure hydrogen flow at 500°C for 1 hour and a continuous flow fixed-bed catalytic reactor operated between reaction temperatures 100° to 500°C and at GHSV of 32,000 hour⁻¹ was used for activity study. Hydrogen reduction caused the Cr-ZSM-5 catalyst to loss about 18% of its crystallinity while more mesopores were created. With reduced Cr-ZSM-5 conversions of 2,000 ppm of ethyl acetate and benzene were found to slightly decrease while marked increase in yield of carbon dioxide was demonstrated. Hydrogen reduction resulted in the migration of chromium ions to form nanoparticles at the external surface of the crystallites and/or in the pore intersections. Changes in catalytic activity with different oxidation states of chromium were in line with the Mars van-Krevelen model. Two Brønsted acid sites reacted in a hydroxylation reaction to give rise to two types of Lewis acid sites during thermal treatment, but only one type of Lewis acid sites created upon reaction with hydrogen. Less amount of coke accumulated on reduced Cr-ZSM-5 was ascribed to higher yield of carbon dioxide and lower concentrations of the Brønsted acid sites on the catalyst.

Keywords

VOC, decomposition, Cr-ZSM-5, H₂ reduction, oxidation states, acidity, coke.

INTRODUCTION

In catalyst preparation procedure, hydrogen reduction is commonly adopted to reduce the catalyst active metal species to the lowest possible oxidation states (1). Metal species with lower oxidation states have been reported to be more active for VOC complete oxidation (1,2). In metal exchange zeolites, metal species normally presents in the form of cations balancing the negatively charged zeolite framework. The reduction of zeolitic cations especially at low loading or in a high-silica zeolite is frequently reversible as described below.



in which M is the metal species and Z represents the zeolite.

Dégé et al (2) found that hydrogen reduction at 300°C for 1 hour increased the activity of Pd/HFAU for *o*-xylene complete oxidation. This suggested that Pd⁰ species was very active and the activation of oxidation with time on stream could be due to an increase in the number of Pd⁰ species by reduction of Pd²⁺ and PdO species by *o*-xylene. Kühl (1) concluded that the reduction of Cu²⁺ in Cu²⁺Y proceeded via a two-step mechanism. The first step was to Cu⁺ that was complete within 1 hour at 200°C and was completely reversible. The second step occurred at higher temperatures when Cu⁺ was reduced to copper crystallites, which could

grow to a size of 300Å. These larger crystallites on the external surface of the zeolite crystals were reoxidized slowly to CuO, while small metal particles within the pore of the zeolite crystals were reoxidized readily to Cu²⁺ ions located in ion-exchange sites. Reports on the effect of reduction of chromium species that can present as Cr²⁺, Cr³⁺ and Cr⁶⁺ when exchanged with zeolites are quite scanty despite being reported as the most active transition metal (3,4) for VOC decomposition process.

The reduction of metal exchanged zeolites also causes certain zeolitic acid sites to be generated. At high cation loadings, destabilization of the zeolite upon reduction results, particularly if the Si/Al is low (2). Depending on reduction conditions, individual metal atoms or metal clusters can be formed. It has been reported that Ni²⁺ and Ag⁺ formed metal crystallites of 240 and 170Å in average size, respectively (1). Therefore, it might be suggested that nickel and silver entities must have migrated in order to aggregate on the external surface of the zeolite crystals, unless the zeolite framework is, at least locally destroyed.

In this study, ethyl acetate and benzene were used as VOC model compounds based on differences in their chemical nature and roles in environmental VOC pollution. Chromium was selected to be metal exchanged with ZSM-5 zeolite to produce a catalyst of high activity, high stability and less coking tendency.

The main objectives of this study were to elucidate and relate changes in the catalytic activity of the Cr-ZSM-5 with physicochemical changes upon reduction with hydrogen.

MATERIALS AND METHODS

Preparation of Cr-ZSM-5

Chromium exchanged ZSM-5 (Si/Al=240) was prepared in two steps. In the first step, NH_4^+ exchange of H-ZSM-5 (Si/Al=240) was performed in 2.25 M of NH_4Cl solution for 6 hours. The metal exchange step was done in acidified (to pH 4) aqueous $\text{Cr}(\text{NO}_3)_3$ solution at 0.086 mol/l, for 6 hours followed by filtration, drying and calcination at 500°C for 6 hours. Before used in the reactor, the catalyst was pelletized, crushed and sieved between 0.25-0.30 mm. Hydrogen reduction on Cr-ZSM-5 was conducted under 100 ml/min of pure hydrogen at 500°C for 1 hour.

Experimental Setup

The catalytic activity test and the preparation of coked Cr-ZSM-5 samples were performed in an 11 mm i.d. glass reactor charged with 0.2g of zeolite catalysts (Figure 1). VOC-laden air stream as feed to the reactor was generated by bubbling nitrogen gas through the VOC saturators. Another flow of high purity air was used to make up the total flow rate to give the desired GHSV. The accurate control of flow rate was achieved by means of Aalborg (AFC 2600) mass flow controllers.

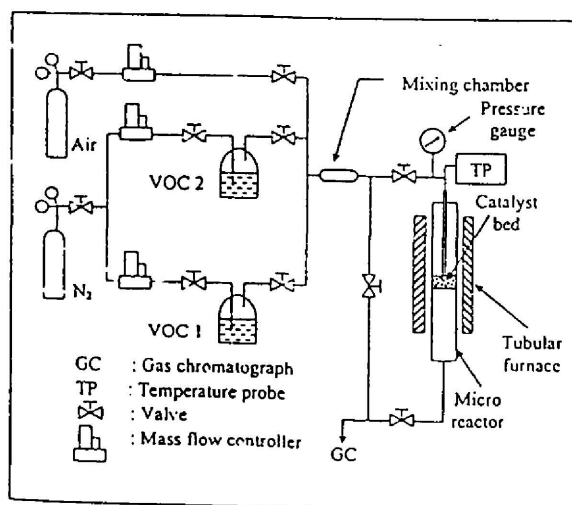


Figure 1: Schematic diagram of the reactor system used in this study.

In order to prepare coked Cr-ZSM-5 samples, feed containing 32,000 ppm of ethyl acetate or benzene was passed through the reactor at reaction temperature of 400°C and GHSV of 3,800 hour^{-1} for 12 hours. In the activity study, the reactor was operated at GHSV of 32,000 hour^{-1} . The feed and product gases were analyzed using an off-line Shimadzu GC-8A gas chromatograph. Porapak Q column was used for separation of carbon

dioxide and organic components while the separation of carbon monoxide was achieved by means of a Molecular Sieve 5A column.

The catalyst characterization

The catalyst sample was characterized for surface characteristics and adsorption-desorption isotherms using Quantachrome Autosorb-1, metal loading using Shimadzu AA-6650 atomic absorption spectroscopy, and crystallinity using Siemens D2000 X-ray diffractometer. Thermogravimetry experiments on coked Cr-ZSM-5 were performed using Perkin Elmer TGA7 thermogravimetry analyzer under pure oxygen flow at 20 ml/min and at temperature ramping rate of 10°/min. Acidity profile of the samples was determined using Chembet 3000 thermal programmed desorption (TPD). Infrared spectroscopy characterization of coked samples was performed using Perkin Elmer 2000 FTIR system. In acid site characterization, prior to scanning with FTIR the samples were adsorbed with pyridine and desorbed at 150°C for 1 hour.

EXPERIMENTAL RESULTS AND DISCUSSION

The catalyst characteristics

The characteristics of Cr-ZSM-5 catalyst before and after hydrogen reduction as compared to its H-form are as shown in Table 1.0. An increase in mesopore area but at the expense of micropore area was detected after chromium exchange. Cr-ZSM-5 experienced subsequent 15% increase in mesopore areas upon reduction with hydrogen. Chromium exchange was also found to cause 4 % drop in relative crystallinity, mainly ascribed to heat treatment in the preparation procedure while hydrogen reduction caused further drop of about 18%. All of these effects signified partial removal of ZSM-5 framework atoms as a result of these two treatments.

Table 1: Characteristics of Cr-ZSM-5 catalysts as compared to its parent H-form.

Characteristics	H-ZSM-5	Cr-ZSM-5 (without H_2 reduction)	Cr-ZSM-5 (with H_2 reduction)
S_{BET} (m^2/g)	393	366	352
Micropore area (m^2/g)	321	272	244
Mesopore area (m^2/g)	72	94	108
Mean pore diameter (Å)	22.5	22.8	23.0
Chromium loading (%)	-	0.98	0.98
*Relative crystallinity (%)	100	96	78

*Relative to parent ZSM-5

Adsorption and desorption isotherm

Changes in the characteristic of pore system brought about by chromium exchange and hydrogen reduction

can be monitored from nitrogen adsorption-desorption isotherms as depicted in Figure 2.0. Clearer hysteresis loop was demonstrated by Cr-ZSM-5 as compared to that of H-ZSM-5. With reduced Cr-ZSM-5, the loop was more noticeable, coupled with steeper adsorption isotherm at higher pressures. This was a typical characteristic in isotherm normally encountered with ink-bottle-shaped pore mouths or with the presence of bottlenecks (5) in the samples pore system.

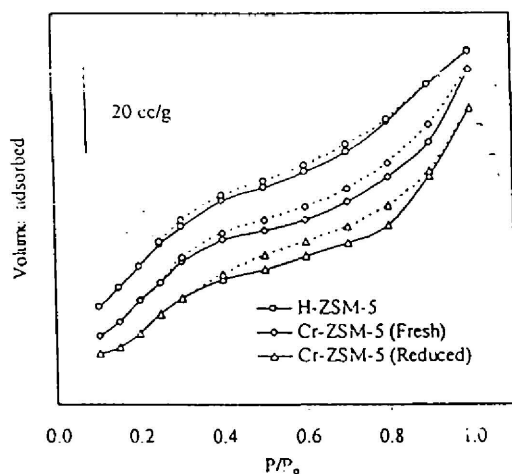


Figure 2: Adsorption (solid line) and desorption (dotted line) isotherms of H-ZSM-5, fresh Cr-ZSM-5 and reduced Cr-ZSM-5.

The exchanged metal ions in zeolite are not fixed to certain exchanged sites but quite mobile especially at high temperatures (1). Hydrogen reduction might have caused the reduced chromium atoms to migrate and aggregated to form metal clusters or nanoparticles (6) on the pore intersections and/or external surface of the ZSM-5. This aggregation might be stopped by the geometry of the pores and/or prolonged in the extra-crystalline region where no geometric obstacles occurred for further growth.

The amount of chromium ion that migrated to the external surfaces and intersections determined maximum size of the metal clusters formed. The ink-bottle-shaped pore mouth occurred when the openings were partially blocked. In the worst case, total blockage rendered some of the active sites inaccessible for reactants. As the pore size of ZSM-5 was only 5.5 Å, this phenomenon would affect the internal mass transfer diffusion to some of the internal surface area, and, coupled with reduced internal active catalytic sites, reduction in catalytic activity should be the likely consequences.

Catalytic activity study

In agreement with conclusions drawn from results shown in Figure 2, reduced Cr-ZSM-5 demonstrated lower ethyl acetate and benzene conversions as evident in Figure 3.0(a). With reduced Cr-ZSM-5, increases of about 15°C and 40°C in the temperature required to achieve 50% conversion (T_{50})

were demonstrated for ethyl acetate and benzene respectively. Marked increase in yield of carbon dioxide was however detected for both organic pollutants as shown in Figure 3.0(b). For both reduced and unreduced Cr-ZSM-5, acetic acid, acetaldehyde, formic acid, formaldehyde and carbon monoxide constituted products of incomplete decomposition in the outlet stream while for benzene, the only carbon containing compounds detected were carbon monoxide and carbon dioxide.

Figure 3.0(b) suggests that reduced chromium species within ZSM-5 matrix were more efficient in completing the VOC oxidation process to produce carbon dioxide. It was postulated that Cr^{3+} as originally found on the catalyst after metal exchange was reduced by hydrogen to Cr^{2+} or even Cr^0 . When the reduced Cr-ZSM-5 was placed in the reactor, in the presence of excess of oxygen in the reaction environment, these two chromium species were oxidized to stabilize at the highest oxidation state i.e. +6 (CrO_3) as the enthalpy of formation of this species was the lowest ($\Delta_f H^\circ = -292.88 \text{ KJ/mol}$) compared to CrO (188 KJ/mol) and CrO_2 (-75.31 KJ/mol).

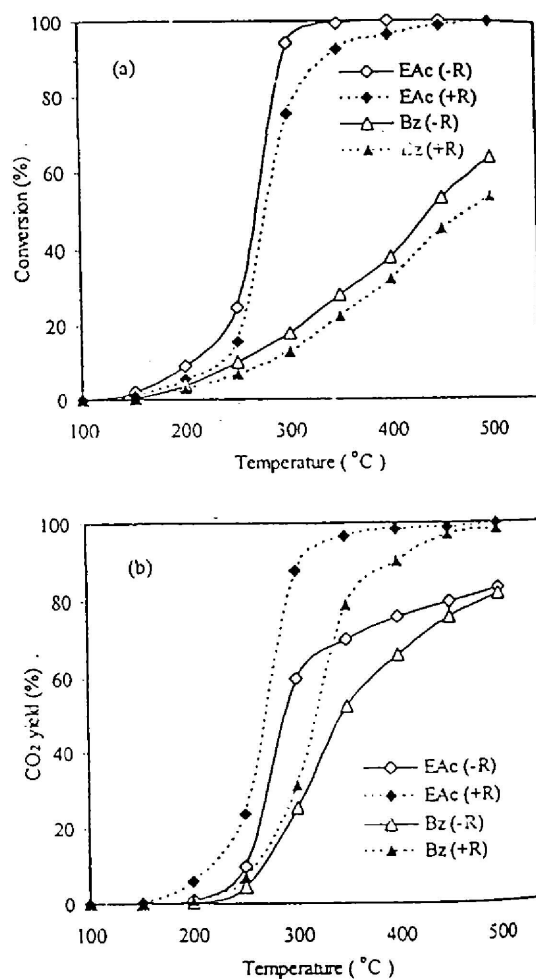
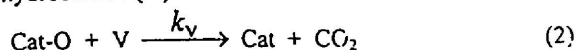


Figure 3: Profile of (a) conversion and, (b) carbon dioxide yield in the decomposition of ethyl acetate (EAc) and benzene (Bz) over Cr-ZSM-5 without (-R) and, with (+R) hydrogen reduction.

Only minimal decrease was detected in the organics conversion as not all of the chromium species found on the zeolite were reduced to lower oxidation states. Study by Dágé et al. (2) concluded that the effect of hydrogen reduction was more significant on metal atoms located in the external surfaces of the zeolite crystallites. Therefore, chromium atoms in the internal pores were either not reduced by hydrogen or underwent a reversible reaction to go back to their original oxidation states (1). The mobility of chromium ion species also played some significant role in determining the extent of hydrogen reduction effect.

As suggested by the Mars van-Krevelen Model that was regarded as the most suitable model to represent VOC oxidation process (7,8), VOC catalytic decomposition can be assumed to occur in two redox steps.

- a) Reduction of the oxidized catalyst (Cat-O) by the hydrocarbon (V):



- b) Oxidation of the catalyst by oxygen from the gas phase:



At oxidation state of +6. (Cr^{6+}), chromium could repeatedly oxidize VOC molecules or the intermediates (Step 1) before reaching the ground oxidation states (probably Cr^0). This explains higher yield of carbon dioxide upon reduction of Cr-ZSM-5 with hydrogen.

Effect of hydrogen reduction on acid sites and coking

Profiles of NH_3 desorption were used to detect changes in acidity of ZSM-5 upon chromium exchange and hydrogen reduction. As depicted in Figure 4, chromium exchange was found to reduce the acidity of ZSM-5 as reflected by a reduction in peak area. It worth noting in the figure that NH_3 desorption started at lower temperatures indicating the emergence of weaker acid sites after chromium exchange. Upon reduction by hydrogen, significant decrease in the acidity of Cr-ZSM-5 was detected.

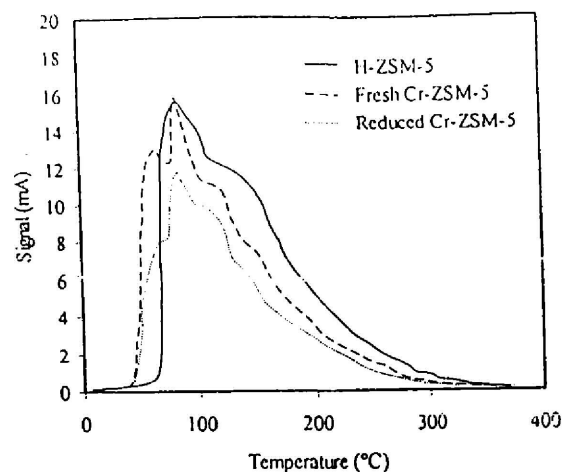


Figure 4: Profile of NH_3 desorption with temperature for H-ZSM-5, fresh Cr-ZSM-5 and reduced Cr-ZSM-5.

Total acidity of zeolites is mostly contributed by Brønsted acid sites (9). In chromium exchange process, some of these acidic OH groups were generally used for exchange (10), leading to some decrease in the acidity. Since in the exchange process, partial atomic removal from ZSM-5 framework as indicated by crystallinity drop occurred, the presence of non-framework silica-alumina debris created some weak acid sites (Lewis acid sites). Marked decrease in acidity after hydrogen reduction suggested the elimination of certain acidic OH groups from reaction with hydrogen. Judging from the acidity profile that maintained the similar shape, it could be said that both Brønsted and Lewis acid sites were affected upon reduction with hydrogen.

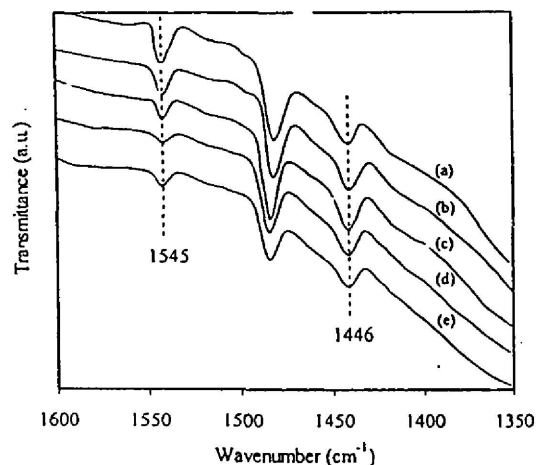


Figure 5: Infrared spectra of pyridine-chemisorbed, (a) H-ZSM-5, (b) fresh Cr-ZSM-5, (c) Cr-ZSM-5 with H_2 reduction, (d) Cr-ZSM-5 after coking with ethyl acetate, and (e) Cr-ZSM-5 after coking with benzene.

Figure 5 confirms that chromium exchange created more Lewis acid sites as indicated by more intense peaks at 1446 cm^{-1} . However, peak corresponding to Brønsted acid sites at 1545 cm^{-1} appeared to be negatively

affected. Therefore, hydrogen reduction on Cr-ZSM-5 created more Lewis acid sites with corresponding partial elimination of Brønsted acid sites.

Upon coking with ethyl acetate and benzene, disappearance of Brønsted and acid sites was detected with more severe effect showed by Cr-ZSM-5 coked with ethyl acetate. Lewis acid sites were, however, less affected suggesting preferential deposition of coke on Brønsted acid sites.

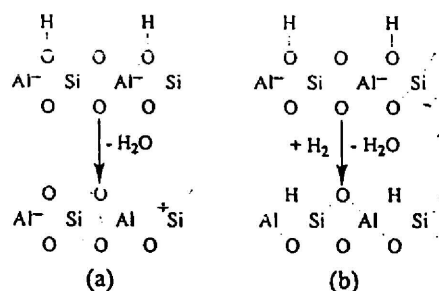


Figure 6: Reaction schemes of ZSM-5 dehydroxylation due to (a) thermal treatment, and, (b) reaction with hydrogen.

Upon thermal treatment, changes in the concentration of Brønsted and Lewis acid sites are explained by Reaction Scheme (a) in Figure 6. In the dehydroxylation reaction, two Brønsted acid sites reacted to give two types of Lewis acid sites, namely the trigonal Al and Si atoms, so that all Al were intra-lattice in the resulting material.

Elimination of acidic OH groups also occurred upon reaction with hydrogen as shown in Reaction Scheme (b) in Figure 6. Here, only one type of Lewis acid sites i.e. trigonal Al resulted from the disappearance of Brønsted acid sites. Thus, the effect of reaction with hydrogen was more significant in reducing the acidity of Cr-ZSM-5 catalyst. Subsequent elimination of Lewis acid sites could be due to the formation of hydrides of Al or Si, thus, creating defects and extraframework species.

Coking behaviour of reduced Cr-ZSM-5

Results of thermogravimetric analysis as summarized in Table 2.0 reveal that more coke deposited on Cr-ZSM-5 catalyst upon coking with ethyl acetate compared to benzene. This could be due to the higher stability of benzene to undergo decomposition over Cr-ZSM-5, thus, forming lesser coke precursors. Reduced Cr-ZSM-5 apparently demonstrated lower tendency toward coking for both ethyl acetate and benzene.

Table 2: Coke content of Cr-ZSM-5 without and with hydrogen reduction.

H ₂ reduction	Coke content (wt. %)*	
	EAc	Bz
Without	5.33	4.96
With	4.64	4.22

*After exposing to 32,000 ppm of respective VOC at 400°C for 12 hours.

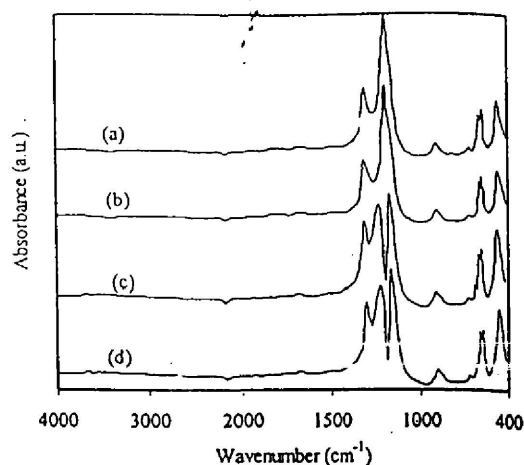


Figure 7: Effect of hydrogen reduction on infrared absorbance of coke from ethyl acetate (EAc) and benzene (Bz) reactions. (a) EAc with unreduced Cr-ZSM-5, (b) EAc with reduced Cr-ZSM-5, (c) Bz with unreduced Cr-ZSM-5 and (d) Bz with reduced Cr-ZSM-5.

The lower tendency toward coke accumulation of the reduced Cr-ZSM-5 could be due to lower number of Brønsted acid sites to host coking reactions. Lower activity of reduced Cr-ZSM-5 also rendered lower organic conversion, hence, lower concentration of coke precursors.

Coke resulted from ethyl acetate reaction presented characteristic absorption bands at 1,110 cm⁻¹ and 1,230 cm⁻¹ while that from benzene had additional band at 1,144 cm⁻¹ as shown in Figure 7. These infrared spectra suggested that reduced Cr-ZSM-5 did not result in any major composition difference compared to unreduced one.

It can be inferred from Figure 7 that coking mechanisms were independent of the types metal species sitting on the catalyst. Therefore, it could be inferred that only acid sites were involved in coke formation process. The lower activity of reduced Cr-ZSM-5 only gave rise to less coking precursors to eventually result in less coke formation. Lower number of available Brønsted acid sites also constrained the coke formation on this catalyst while Lewis acid sites had no or little contribution toward this process.

CONCLUSIONS

Hydrogen reduction caused the Cr-ZSM-5 to lose about 18% of its crystallinity while more mesopores were created. With reduced Cr-ZSM-5, the conversions 2,000 ppm of ethyl acetate and benzene were found slightly decrease while marked increase in yield carbon dioxide was demonstrated. Hydrogen reduction treatment might have caused the migration of chromium species to form nanoparticles at the external surface the ZSM-5 crystallites or in its pore intersections, changes in catalytic activity with different oxidation

states of chromium atom were in line with Mars van-Krevelen model. Two Brønsted acid sites reacted in a hydroxylation reaction to give rise to two types of Lewis acid sites during thermal treatment, but only one type of Lewis acid sites was created upon reaction with hydrogen. Less amount of coke accumulated on reduced Cr-ZSM-5 was attributed to higher yield of carbon dioxide and lower concentration of Brønsted acid sites on the catalyst with no regard to types of chromium species found in Cr-ZSM-5.

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