PILLARED CLAYS AS SUPERIOR CATALYSTS FOR SELECTIVE CATALYTIC REDUCTION OF NITRIC OXIDE

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Abstract

Selective catalytic reduction (SCR) of NO_x by hydrocarbons was investigated on Pt doped MCM-41 and copper ion and/or cerium ion-exchanged Al-MCM-41 in the presence of excess oxygen. It was found that Pt/MCM-41 provided the highest specific NO reduction rates as compared with other Pt doped catalysts reported in the literature, such as Pt/Al_2O_3 and Pt/ZSM-5. For different hydrocarbons, the catalytic activity decreased according to the sequence of $C_3H_6 \approx C_2H_4 >> C_3H_8 > CH_4$. This catalyst was also stable in the presence of H_2O and SO_2. Cu exchanged Al-MCM-41 and cerium promoted Cu-Al-MCM-41 (i.e., Ce-Cu-Al-MCM-41) were also found to be active in this reaction. Higher NO_x conversions to N_2 were obtained on the Ce-Cu-Al-MCM-41 as compared with Cu-Al-MCM-41. The activity of Ce-Cu-Al-MCM-41 was approximately the same as that of Cu-ZSM-5; but the former had a wider temperature mindow. TPR results indicated that only isolated Cu^{2+} and Cu^{+} ions were detected in the Cu^{2+}-exchanged Al-MCM-41 samples, which may play an important role in the selective catalytic reduction of NO_x to N_2. After some cerium ions were introduced into Cu-Al-MCM-41, Cu^{2+} in the molecular sieve became more easily reducible by H_2. This may be related to the increase of catalytic activity of NO_x reduction by ethylene.

1. Introduction

Removal of NO_x (NO + NO_2) from exhaust gases is a challenging subject which has been extensively studied in recent years. The selective catalytic reduction (SCR) of NO_x is one of the most effective means. For large power plants, V_2O_5/TiO_2 has been the main commercial catalyst for SCR with NH_3 for stationary sources [1]. However, for diesel- and gasoline-fueled engines in vehicles, the use of NH_3-based SCR technologies is not practical because of the high cost and NH_3 handling problems. The three-way catalyst has been used commercially in gasoline engines for reduction NO to N_2 by carbon monoxide and hydrocarbons under rich-burn conditions, but it becomes ineffective in the presence of excess oxygen [2]. The first catalyst found to be active for selective catalytic reduction of NO by hydrocarbons in the presence of excess oxygen was copper exchanged ZSM-5, reported in 1990 by Iwamoto et al.[3] and Held et al.[4]. A large number of catalysts have been found to be active for these reactions since 1990, such as Cu-ZSM-5 [3-6], Co-ZSM-5 and Co-Ferrierite [7-9], Co/Al2O3[10], Ce-ZSM-5 [11], Cu^{2+}-exchanged pillared clay [12, 13], Fe-ZSM-5 [14], Pt-ZSM-5 [15], Rh-ZSM-5 [16], Pt/Al_2O_3 [17-19], and supported Ag[20]. Although Cu-ZSM-5 is very active and the most intensively studied catalyst, it suffers from severe deactivation in engine tests, mainly due to H_2O and SO_2 [21, 22]. By comparison, Pt-ZSM-5 was found to be more active than Cu-ZSM-5 and Fe-MOR at lower temperatures (127-277 °C) [14] and the catalysts containing Pt were stable in real diesel exhaust [23]. But they produced much N_2O.

MCM-41, a new member of the zeolite family, shows a regular hexagonal array of uniform pore openings with pore dimensions between 1.5 and 10 nm [24, 25]. Because it has high thermal stability, high BET surface areas and large pore volumes, MCM-41 has already attracted considerable interests in recent years. It has been studied as catalysts, support and sorbents[26]. Corma and co-workers [27] reported a good catalytic activity for MCM-41 in selective oxidation of hex-1-ene with H_2O_2, and norbornene with terbutylhydroperoxide on Ti-MCM-41 catalyst. Fe-Al-MCM-41 were also reported by Yang et. al. [28] as a good catalyst for selective catalytic reduction of NO with NH_3. In this work, we investigated the activity of platinum doped MCM-41 and Cu exchanged Al-MCM-41 catalysts in SCR of NO with methane, ethene, propane and propene in the presence of excess oxygen. The effects of oxygen, water vapor and sulfur dioxide on SCR activity were also studied.

2. Experimental

2.1 Preparation of Pt/MCM-41 catalyst

Pure silica MCM-41 was synthesized according to the procedure given by Kim et. al. [29]. 30.1 ml sodium silicate solution (containing 14% of NaOH and 27% of SiO_2, Aldrich) was dropwise added to a three-neck flask containing a mixture of 41.3 ml cetyltrimethylammonium chloride (CTMACl, 25 wt% in water, Aldrich), 0.6 ml 28 wt% NH_3 aqueous solution (J.T. Baker) and deionized water, with constant stirring at room temperature. The resulting gel mixture had the following molar composition: 1 SiO_2 : 0.166 CTMACl : 0.388 Na_2O : 0.0247 NH_4OH : 40 H_2O. After stirring for 1 h, the mixture was heated to 97 °C for 24 h, then cooled down to room temperature and the pH was adjusted to 10.2 by adding 2N HNO_3. The reaction mixture (pH=10.2) was heated to 97 °C again for 24 h. This procedure of pH adjustment and subsequent heating (for 24 h drration) was repeated twice. Finally, the product was filtered, washed with deionized water, dried at 110 °C for 12 h and then calcined at 560 °C for 10 h in a flow of air (150 ml/min). 0.5-5 wt% Pt/MCM-41 catalysts were prepared by using the incipient wetness impregnation method with hydrogen hexachloroplatinate (IV) hydrate (99.9%, Aldrich) as the platinum precursor. After calcination at 500 °C for 4 h in air, the samples were crushed to 60-100 mesh.

2.2 Preparation of Cu-Al-MCM-41 catalyst

Fumed silica (99.8%, Aldrich), tetramethylammonium hydroxide pentahydrate (TMAOH, 97%, Aldrich),), 25 wt.% cetyltrimethylammonium chloride (CTMACl) in water (Aldrich),

$Al[C_2H_5CH(CH_3)O]_3$ (97%, Aldrich) and NaOH (98.1%, Fisher) were used as source materials for preparing Al-MCM-41.

The Al-MCM-41 (Si/Al=10) sample was synthesized according to the procedure given by Borade and Clearfield [37]. Solution A was prepared by dissolving 1.325 g TMAOH in 100 ml deionized water and then adding 5 g fumed silica. Solution B was obtained by dissolving 0.72 g NaOH in deionized water and adding 25 ml CTMACl followed by adding 2.19 ml $Al[C_2H_5CH(CH_3)O]_3$ at room temperature. The two solutions were stirred for 10-15 min, then solution A was added to solution B. The reaction mixture had the following chemical composition $1SiO_2$-$0.05Al_2O_3$-0.23CTMACl-$0.11Na_2O$-0.089TMAOH-$125H_2O$. After being stirred for 15 min, the mixture was transferred into a 250 ml three-neck flask and was then heated at 100 °C for 48 h. After filtering, the solid was washed, dried and calcined at 560 °C for 10 h in a flow of air (150 ml/min).

The copper and cerium ion-exchanged Al-MCM-41 were prepared by using conventional ion exchange procedure at room temperature. Solutions of 0.02 M $Cu(NO_3)_2$ (adjusting pH value to 4.5 by 2N HNO_3) and 0.02 M $Ce(NO_3)_3$ were used for exchange. The Ce-Cu-Al-MCM-41 catalyst was obtained from Cu^{2+} exchange of the Ce-Al-MCM-41 sample; Ce exchange was done first because it was harder than copper exchange. All the exchange processes were repeated three times and each time was carried out for 24 h. After the ion-exchange procedure, all the samples were calcined at 550 °C in air for 4 h. The Cu/Al in the Cu-Al-MCM-41 obtained by neutron activation analysis was 0.372 (i.e., 74.4% ion exchange), and Ce/Al in Ce-Al-MCM-41 was 0.164 (i.e., 49.2% ion exchange). In Ce-Cu-Al-MCM-41 sample, Ce/Al and Cu/Al were 0.053 and 0.37, respectively, i.e., 89.9% total ion exchange.

2.3 Characterization of catalyst

The powder X-ray diffraction (XRD) measurement was carried out with a Rigaku Rotaflex D/Max-C system with CuKα (λ = 0.1543 nm) radiation. The samples were loaded on a sample holder with a depth of 1 mm. XRD patterns were recorded in the ranges of 2θ = 1-10° and 30-70°.

A Micromeritics ASAP 2010 micropore size analyzer was used to measure the N_2 adsorption isotherm of the samples at liquid N_2 temperature (-196 °C). The specific surface areas of the samples were determined from the linear portion of the BET plots (P/P_0 = 0.05-0.20). The pore size distribution was calculated from the desorption branch of the N_2 adsorption isotherm using the Barrett-Joyner-Halenda (BJH) Formula, as suggested by Tanev and Vlaev [30], because the desorption branch can provide more information about the degree of blocking than the adsorption branch hence the best results were obtained from the BJH formula. Prior to the surface area and pore size distribution measurements, the samples were dehydrated at 350 °C for 4 h.

The dispersions of Pt in the Pt/MCM-41 catalysts were measured by CO chemisorption on a thermogravimetric analyzer (TGA, Cahn 2000 System 113). Prior to CO chemisorption, the samples were first reduced by H_2 (5.34% H_2 in N_2) at 400 °C for 5 h or more, followed by cooloing to room temperature in He flow. Chemisorption of CO was performed at room temperature (with 1.03% CO in He). Equilibrium was assumed when no further weight gain was observed. Based on the amount of CO adsorbed and assuming 1:1 ration for Pt_s:CO, Pt dispersions were obtained.

The reducibility of catalyst was characterized by temperature-programmed reduction (TPR) analysis. In each experiment, 0.1 g sample was loaded into a quartz reactor and then pretreated in a flow of He (40 ml/min) at 400 °C for 0.5 h. After the sample was cooled down to room temperature in He, the reduction of the sample was carried out from 30 to 700 °C in a flow of 5.34 % H_2/N_2 (27 ml/min) at 10 °C/min. The consumption of H_2 was monitored continuously by a thermal conductivity detector. The water produced during the reduction was trapped in a 5A molecular sieve column.

2.4 Catalytic Activity

The SCR activity measurement was carried out in a fixed-bed quartz reactor. The reaction temperature was controlled by an Omega (CN-2010) programmable temperature controller. The typical reactant gas composition was as follows: 1000 ppm NO, 1000-3000 ppm hydrocarbons (CH_4, C_2H_4, C_3H_8 and C_3H_6), 0-7.8% O_2, 500 ppm SO_2 (when used), 5% water vapor (when used), and balance He. The total flow rate was 250 ml/min (ambient conditions). The premixed gases (1.01% NO in He, 1.05% CH_4 in He, 1.04% C_2H_4 in He, 1.07% C_3H_6 in He, 0.98% C_3H_8 in He and 0.99% SO_2 in He) were supplied by Matheson Company. The NO and NO_2 concentrations were continuously monitored by a chemiluminescent NO/NO_x analyzer (Thermo Electro Corporation, Model 10). The other effluent gases were analyzed by a gas chromatograph (Shimadzu, 14A) at 50 °C with 5A molecular sieve column for O_2, N_2 , CH_4 and CO, and Porapak Q column for CO_2, N_2O, C_2H_4., C_3H_6 and C_3H_8. Other details of the SCR reaction system was described elsewhere [31].

3. Results and Discussion

3.1 Pt/MCM-41 catalyst

The XRD pattern of pure MCM-41 (not shown) consisted of one very strong peak at $2\theta = 2.14^\circ$ and three weak peaks at $2\theta = 3.77^\circ$, 4.31° and 5.79°, which can be indexed, respectively, to (100), (110), (200) and (210) diffraction peaks characteristic of a hexagonal structure of MCM-41 [24, 25, 29]. According to the value of d_{100} ($d_{100} = 4.14$ nm), the unit cell dimension (a = 4.78 nm) was calculated by using the formula: $a = 2d_{100}/\sqrt{3}$. After platinum dopings on the MCM-41 sample, the XRD patterns were essentially unchanged (Fig.1), indicating that the incipient wetness impregnation process did not alter the framework structure of this zeolite. The platinum metal phase, with peaks at 2θ of 39.73°, 46.24° and 67.41°, could also be identified in the XRD patterns of the Pt/MCM-41 catalysts. These three peaks were reflections of, respectively, (111), (200) and (220) faces of the cubic platinum metal structure. With increasing amount of platinum, the intensities of these peaks were seen to increase. No platinum oxide phase was detected, whose three strongest peaks would have been found at 2θ of 34.8°, 42.5° and 54.9°. This was most probably due to its good dispersion on the catalysts. The BET specific surface area, pore volume, average pore diameter, platinum dispersion of the Pt/MCM-41 catalysts are summarized in Table 1. The Pt/MCM-41 catalysts were found to have narrow pore size distributions with pore sizes near 3.8 nm, high BET surface areas(> 900 m^2/g) and large pore volumes(> 1.00 cm^3/g). The Pt dispersion obtained by CO chemisorption was between 54% and 24% on the 0.5-5% Pt/MCM-41 catalysts, with higher dispersions for lower Pt amounts.

The catalytic performance of 0.5-5 % Pt/MCM-41 for the reduction of NO with C_3H_6 is shown in Table 2. At lower temperatures(below 200 °C), NO conversion and C_3H_6 conversion were small. With increasing temperature, NO conversion was found to increase at first, passing through a maximum, then decreased at higher temperatures. The maximum NO conversion appeared at the temperature at which propene conversion reached 100%. Carbon dioxide was the only product (beside water) of propene oxidation. The N balance and C balance were above 94% in this work. Similar to other platinum doped or exchanged catalysts reported in the literature, N_2O was the main product. This may be related to the fact that platinum is a poor N_2O decomposition catalyst [19,32]. When the platinum amount increased from 0.5% to 5%, the peak NO conversion temperature decreased from 275 °C to 250 °C. At high temperatures, the loss of catalytic activity was due to the oxidation of C_3H_6 by O_2. The turnover frequencies (TOF) for the conversion of NO, defined as the number of NO molecules converted per surface Pt atom per second, are also given in Table 2. With the increase of platinum amount, the maximum TOF was found to decrease. The steady-state NO reduction rate (mmol/g·h) was calculated as [8]

$$\text{NO reduction rate} = - d[NO]/dt = F_0X / w \qquad (1)$$

where F_0 was inlet molar flow rate of NO, χ was NO conversion and w was weight of the catalyst. The maximum NO reduction rate on these Pt/MCM-41 catalysts were 3.6-4.3 mmol/g·h at 275 or 250 °C, which was higher than 2.8 mmol/ g·h obtained on 1% Pt/Al_2O_3 catalyst [19] under similar conditions.

Hamada et al[17] reported that the activity for SCR decreased significantly when alumina was replaced by silica as the support for Pt. Pt supported on ZSM-5 also showed SCR activity [33]. However, the Pt was doped on the exterior surface of the ZSM-5 crystals, and hence was not an effective support [34]. This indicates that the nature of the support plays an important role in the activity of NO reduction with hydrocarbon on platinum. The high activity obtained on the Pt/MCM-41 catalysts was likely due to the large pores and high surface area of MCM-41. Pore diffusion limitation is known to be significant for the SCR reaction [28].

It is well known that oxygen is important in SCR reactions of NO both by hydrocarbons [34] and by NH_3 [1]. The effect of O_2 on SCR by C_3H_6 over 1% Pt/MCM-41 at 250 °C was studied, and the results are shown in Fig. 2. In the absence of O_2, almost no activity was obtained. When 0.5% of O_2 was added to the reactant gas mixture, NO conversion was found to increase significantly to 88% and C_3H_6 conversion also reached 100% at the same temperature. After that, NO conversion decreased slightly with the increase of O_2 concentration. It is known that reduced platinum atoms play an important role for NO conversion [34, 35]. Burch and Watling reported that about 14% of platinum atoms on the Pt/Al_2O_3 catalyst surface were in the reduced form under the reaction conditions and that NO did not convert to N_2 on a completely oxidized, supported platinum catalyst [18, 35]. In this work, after the Pt/MCM-41 catalysts were calcined at 500°C in air (21% of O_2), the platinum metal phase was still detected by XRD. The XRD result combined with the high dispersions were indirect evidence for the high probability that there existed reduced Pt atoms on the surface. The reduced platinum atoms could be the active sites for NO reduction. The role of oxygen was attributed to its reaction with hydrocarbon fragments left on the Pt sites and thus prevention of the deactivation of the active sites by coke formation[34].

In order to compare directly the effect of different hydrocarbons on SCR activity of NO, we also studied the catalytic performance on the 1% Pt/MCM-41 sample using CH_4, C_2H_4 and C_3H_8 as reductants at the same carbon concentration condition, i.e., 3000 ppm of CH_4, 1500 ppm of C_2H_4 and 1000 ppm of C_3H_8, as compared with 1000 ppm of C_3H_6. The results are shown in Fig. 3-6. For CH_4 and C_3H_8, no or little activity for NO reduction was found on the 1% Pt/MCM-41 catalyst in the temperature range of

150-450 °C (Fig. 3 and Fig. 5). At higher temperatures, only a small amount of CH_4 was oxidized to CO_2 by O_2, while a large amount of C_3H_8 was converted to CO_2 by O_2. By comparison, a very high activity was obtained when C_2H_4 and C_3H_6 were used as the reductants (Fig. 4 and Fig.6). The maximum NO conversion reached 81% at 225 °C. This indicated that C_2H_4 and C_3H_6 were excellent reductants but CH_4 and C_3H_8 were poor reductants for SCR of NO over the Pt/MCM-41 catalyst. Similar phenomenon was observed on Pt/Al_2O_3 and Pt/SiO_2 catalysts [36]. This difference is related to the nature of these hydrocarbons. Ethene and propene have a C=C double bond and are easy to adsorb on platinum atoms and thus result in a high converage of these alkene species. So the surface is readily reduced to Pt atoms. However, methane and propane are saturated hydrocarbons and thus must have the C-H bond broken to chemisorb on the Pt surface. So adsorbed oxygen is the predominant surface species [36]. Because the C-H bond energy in the CH_4 molecule (105 kcal/mol) is larger than that in C_3H_8 molecule (95 kcal/mol), a higher C_3H_8 conversion was obtained using C_3H_8 as the reductant than that using CH_4 as the reductant in the high temperature range. It is not surprising that Pt and PtO might have different catalytic properties for SCR reaction of NO on platinum doped catalysts. Ethene and Propene are better reductants than methane and propane on the Pt/MCM-41 catalyst.

The effect of H_2O and SO_2 on SCR activity of NO with C_3H_6 on 1% Pt/MCM-41 catalyst is shown in Fig.7. The result exhibited that the Pt/MCM-41 catalyst was a stable catalyst. After being on stream for 10 h at 225 °C, under the conditions of 1000 ppm NO, 1000 ppm C_3H_6, 2% of O_2, He as balance and 250 ml/min of total flow rate, NO conversion remained at 80-81%. When 5% water vapor and 500 ppm SO_2 were added to the reactant gas, the catalytic performance remained unchanged in the following 4 h at 225 °C.

3.2 Cu-Al-MCM-41 catalyst

3.2.1 Characterization of catalyst

The powder XRD patterns of Al-MCM-41 and ion-exchanged Al-MCM-41 samples are shown in Fig. 8. The pattern of Al-MCM-41 is consistent with that reported previously for the Al-MCM-41 molecular sieve [37] and all XRD peaks can be indexed on a hexagonal lattice with d_{100} = 4.1 nm. According to the value of d_{100}, the unit cell dimension (a=4.7 nm) was calculated by the formula $a= 2d_{100}/\ \ 3$. After the sample was exchanged with copper ions and/or cerium ions, the shapes of XRD patterns were essentially unchanged, indicating that the ion exchange process did not affect the framework structure of this molecular sieve. No oxide phase (CuO or Ce_2O_3) was detected in these samples.

The BET specific surface area, pore volume, average pore diameter of the Al-MCM-41 and ion-exchanged Al-MCM-41 samples are summarized in Table 3. These samples were found to have narrow pore size distributions with pore size of ca. 4.2 nm, high BET specific surface areas (ca. 900 m^2/g) and high pore volumes (> 1.00 cm^3/g).

TPR can be used to identify and quantify the copper species in copper ion-exchanged zeolite [38]. As shown in Fig. 9, no H_2 consumption was found on the Ce^{3+}-exchanged Al-MCM-41 sample below 700 ^{o}C, indicating that the Ce^{3+} in the framework of Al-MCM-41 is very hard to be reduced to lower valence. For Cu-Al-MCM-41 and Ce-Cu-Al-MCM-41 samples, the TPR profiles showed two reduction peaks, which suggests a two-step reduction process of isolated Cu^{2+} species [38]. One peak appeared at a lower temperature, indicating that the process of $Cu^{2+} \rightarrow Cu^{+}$ occurred. The other peak at a higher temperature suggests that the produced Cu^{+} was further reduced to Cu^{0}. According to these results, we can conclude that no CuO aggregates existed in the two copper ion-underexchanged Al-MCM-41 samples (i.e., Cu/Al < 0.5) because the CuO aggregates would be reduced to Cu^{o} by H_2 in one step at about 230 ^{o}C if they existed in the two samples [38]. This was in line with the above XRD result that no CuO phase was detected in the two samples. Copper in the Cu-Al-MCM-41 and Ce-Cu-Al-MCM-41 mainly existed in the form of isolated copper ions. Delahay et al. also reported that copper was mainly present as isolated Cu^{2+} species in underexchanged Cu-Beta and Cu-MFI zeolites [38]. The ratios of H_2 consumption to Cu for the second peak ($Cu^+ \rightarrow Cu^0$) in the two samples were close to 0.5 (Table 3); by comparison, the H_2/Cu ratios for the first peak ($Cu^{2+} \rightarrow Cu^+$) were lower than 0.5 (Table 3). This phenomenon could be accounted for as the result of partial reduction of Cu^{2+} to Cu^+ during the course of catalyst preparation (calcination at 550 °C) or pretreatment at 400 °C in a flow of He. In addition, the reduction temperatures of Ce-Cu-Al-MCM-41 were about 20 °C lower than those of Cu-Al-MCM-41 (323 °C vs. 342 °C and 540 °C vs. 561 °C, as shown in Fig. 9), suggesting that the Cu^{2+} and Cu^+ ions in the former are more easily reduced than those in the latter. This is reasonable because when Na^+ in the Al-MCM-41 was partially substituted by Ce^{3+}, the positive charges in the framework would increase and thus lead to weaker electrostatic interactions between Al-MCM-41 and the copper ions. As expected, this would also result in a lower Cu^{2+}/Cu^+ ratio in the Ce-Cu-Al-MCM-41 than that in the Cu-Al-MCM-41 (0.73 vs. 0.80, as shown in Table 3) after the samples were treated at 400 °C in He.

3.2.2 NO_x reduction activity of catalyst

The catalytic performance of the catalysts for SCR reaction of NO_x with C_2H_4 as functions of the reaction temperature are summarized in Fig. 10 and Fig. 11. Ce^{3+}-exchanged Al-MCM-41 was found to be inactive in this reaction at 250-600 °C; almost no NO_x was reduced to N_2, but some C_2H_4 was oxidized to CO_2 by O_2 at higher temperatures. Over the Cu-Al-MCM-41 and Ce-Cu-Al-MCM-41 catalysts, only a small amount of NO_x was converted to N_2 at 250 °C. With the increase of reaction temperature, NO_x conversion increased, passing through a maximum, then decreased at higher temperatures. No nitrous monoxide and carbon monoxide were detected in the temperature range and N_2 was the only product containing nitrogen. The nitrogen balance and carbon balance were both above 95% in this work. The decrease in NO_x conversion at higher temperatures was due to the combustion of ethylene. Ce-Cu-Al-MCM-41 always showed higher NO_x conversions than Cu-Al-MCM-41, indicating that cerium ions played an important promoting effect in the catalyst (because no activity was obtained on Ce-Al-MCM-41 sample). The maximum NO_x conversion reached 38% at 550 °C over the Ce-Cu-Al-MCM-41 catalyst, which was about 15% higher than that over Cu-Al-MCM-41. The ethylene conversion reached 100% at 500 °C on Cu-Al-MCM-41 catalyst. The conversions of ethylene on Ce-Cu-Al-MCM-41 were found to be lower than those on Cu-Al-MCM-41 before they reached 100% (Fig. 11).

It is well known that oxygen is important in the SCR reaction of nitric oxides by hydrocarbons. The effect of O_2 concentration on NO_x conversion to N_2 was also investigated at 500 °C on Ce-Al-Cu-MCM-41 catalyst. As shown in Fig. 12, almost no NO_x reacted with ethylene in the absence of O_2. After O_2 was introduced into the feed mixture, NO_x conversion was significantly increased. This indicates that oxygen plays an important role for the reduction of NO_x by C_2H_4, as we expected. The maximum conversion reached ca. 38% in the presence of 1-1.6% O_2 . After that, NO_x conversion was found to decrease slightly at higher O_2 concentrations. C_2H_4 conversion always increased with the increase of O_2 concentration.

The effect of H_2O and SO_2 on the catalytic activity of the Ce-Cu-Al-MCM-41 catalyst was also studied in this work. As shown in Fig. 13, the Ce-Cu-Al-MCM-41 was stable in the absence of H_2O and SO_2. However, when 2.3% water vapor and 500 ppm SO_2 were added to reaction gases, the NO_x conversion was found to decrease from 36% to 21-22% at 500 °C on the catalyst. No deterioration of catalyst was observed after 30 min of running under these conditions. The effect of H_2O and SO_2 was reversible. When H_2O and SO_2 were removed from the reactants, the catalytic activity was restored.

3.2.3 Discussion

When sodium ions in Al-MCM-41 were partially exchanged by copper ions or copper and cerium ions, the Cu-Al-MCM-41 and Ce-Cu-Al-MCM-41 catalysts showed a high activity in SCR reaction of NO_x by ethylene in the presence of excess oxygen. Since the samples without copper (i.e., Al-MCM-41 and Ce-Al-MCM-41) showed little or no activity in this reaction, copper ions clearly play an important role for the reduction of NO_x to N_2. Iwamoto and co-workers studied the effect of zeolite structure on the catalytic performance of SCR reaction by comparing NO_x conversion on different zeolites that were subjected to copper ion exchange [3]. In addition to Cu-ZSM-5 (Si/Al = 11.7), Cu^{2+}-exchanged ferrierite (Si/Al = 6.2), mordenite (Si/Al = 5.3), Zeolite L (Si/Al = 3.0) and Zeolite Y (Si/Al = 2.8) were also investigated. They found that the maximum activity was obtained on Cu-ZSM-5 and the lowest activity was on Cu-Y. The maximum NO_x conversion (ca. 40%) was obtained on the Cu-ZSM-5 at 250 ^oC under the conditions of catalyst = 0.5 g, [NO] = 1000 ppm, [C_2H_4] = 250 ppm, [O_2] = 2% and total flowrate = 150 ml/min [3]. Delahay et al. [38] and Corma et al. [39] also reported that a similar catalytic activity for NO_x reduction was obtained on Cu-Beta zeolite as compared with Cu-ZSM-5. In this work, we found that Cu-Al-MCM-41 was also active for NO_x reduction to N_2 by ethylene in the presence of excess oxygen, but the activity was lower than that of Cu-ZSM-5. However, on the Ce^{3+} promoted Cu-Al-MCM-41 catalyst, we obtained 38% NO_x conversion at 550 °C, which was close to the maximum value on the Cu-ZSM-5 catalyst under the same conditions, as shown in Fig. 10. The maximum NO_x conversion on the Cu-ZSM-5 was obtained at a lower temperature (300 °C), but Ce-Cu-Al-MCM-41 catalyst had a wider temperature window (i.e., a window of 200 °C vs. 95 °C at NO_x conversion > 25%, as shown in Fig. 10). Like Cu-ZSM-5, the catalytic activity on the Ce-Cu-Al-MCM-41 catalyst decreased in the presence of H_2O and SO_2. The inhibition of catalytic activity by H_2O and SO_2 has been extensively studied on Cu-ZSM-5 catalyst [40-42]. Two reasons were proposed for the deactivation. One was competitive adsorption for the active sites by H_2O and SO_2; the other was framework dealumination of

ZSM-5 after it was subjected to prolonged exposure to wet exhaust gas at high temperatures [40-42]. The former was reversible; the latter was irreversible. It has been reported that Al-MCM-41 has a high hydrothermal stability [30]. For example, it is stable after heating at 800-900 ^oC for 2 h in the presence of 2.3% H_2O/O_2 [30]. In this work, the Ce-Cu-Al-MCM-41 catalyst was only exposed to 2.3% H_2O at 500 ^oC for a short time, hence it was impossible for framework dealumination of Al-MCM-41. The reason for deactivation by H_2O and SO_2 was likely due to competitive adsorption on the copper sites by H_2O and SO_2. Our previous study also showed that SO_2 could adsorb on the same sites as those by NO_x over Cu^{2+}-exchanged pillared clays .

H_2-TPR and XRD results showed that the copper in the Cu-Al-MCM-41 and Ce-Cu-Al-MCM-41 was mainly present in the form of isolated Cu^{2+} ions. Cu^{2+} ions could be partially reduced to Cu^+ ions when the samples were treated at high temperatures. Almost no CuO aggregates were detected in the two catalysts. This is consistent with the results obtained in other zeolites (e.g., ZSM-5, Beta zeolite, etc.) that were underexchanged by Cu^{2+} [38]. The isolated Cu^{2+} ions may play an important role in the SCR reaction of NO_x by ethylene. Several authors have claimed that the active species for SCR reaction of NO_x may involve a Cu^{2+}/Cu^+ redox cycle in Cu^{2+}-exchanged zeolites [38, 39, 43]. In the presence of hydrocarbon (e.g., C_2H_4, C_3H_6, C_3H_8, etc.), the Cu^{2+} would be reduced to Cu^+ and then Cu^+ was oxidized back to Cu^{2+} by NO_x, thus completing the catalytic cycle. The X-ray absorption near edge structure (XANES) study of Liu and Robota [43] reported that a significant proportion of copper was in the form of Cu^+ in the presence of propylene (one of the selective reducing agents), even in a large excess of oxygen. Furthermore, the concentration of cuprous ions followed the same trend with temperature as that of NO_x conversion in the reaction. But the use of non-selective reducing agent (e.g., methane) did not lead to the formation of Cu^+. Hence, they concluded that cuprous ions are essential for this reaction. However, more recently, Haller and coworkers [44] used *in situ* XANES analysis together with comparison of the catalytic behaviors of Cu-ZSM-5 with CuO/Al_2O_3 and CuO/SiO_2 systems and indicated that the rate limiting step of the reaction took place on cupric oxides. They suggested that zeolite supports did not play an essential role in the reaction and that the mechanism might not involve a Cu^{2+}/Cu^{+} redox cycle. Their conclusions were based on the fact that the CuO/Al_2O_3 sample showed a higher activity in the reduction of nitric oxides than the Cu-ZSM-5 under their experimental conditions. On the other hand, reports also exist showing that Cu-ZSM-5 (with high exchange, e.g., 80-100%) was more active than CuO doped Al_2O_3 [34]. In this work, only isolated Cu^{2+} and Cu^{+} ions were detected in Cu-Al-MCM-41 and Ce-Cu-MCM-41 catalysts, suggesting that CuO aggregates may not play an important role in this reaction on these two catalysts. After some cerium ions were introduced into Cu-Al-MCM-41, copper ions in the molecular sieve become more easily reducible by H_2. This may be related to the increase of catalytic activity of NO_x reduction by ethylene.

4. Conclusions

0.5-5 wt% Pt/MCM-41 catalysts were prepared and studied for the selective catalytic reduction of NO with CH_4, C_2H_4, C_3H_6 and C_3H_8 in the presence of excess oxygen. The catalysts had high BET surface areas (> 900 m^2/g) and large pore volumes(> 1.00 cm^3/g). Platinum metal particles were detected in these catalysts at room temperature by XRD. A high activity for NO reduction was obtained when C_2H_4 or C_3H_6 was used as the reductant and the maximum NO reduction rate reached 4.3 mmol/g·h under the conditions of 1000 ppm NO, 1000 ppm C_3H_6, 2% of O_2 and He as balance; but no or little activity was found when CH_4 or C_3H_8 was used. This difference was related to the different nature of these hydrocarbons. The Pt/MCM-41 catalyst showed a good stability. H_2O and SO_2 did not cause deactivation of the catalyst.

Besides Pt/MCM-41, Cu-Al-MCM-41 and Ce-Cu-Al-MCM-41 were also found to be active in the reduction of NO_x to N_2 by ethylene in the presence of excess oxygen. Due to the interaction between cerium and copper, the copper ions in the Ce-Cu-Al-MCM-41 could be reduced by H_2 more easily than those in the Cu-Al-MCM-41. The former also showed higher NO_x conversions than the latter in the temperature range of 250-600 °C. In the copper ion-exchanged Al-MCM-41 catalysts, the copper species were mainly present in the form of isolated Cu^{2+} ions, which may play an important role in the selective catalytic reduction of NO_x to N_2. H_2O and SO_2 caused some deactivation of the catalyst, but the deactivation was reversible.

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Table 1 Platium dispersions and pore structure parameters of the Pt/MCM-41 catalysts

Catalyst	BET Specific Surface Area (m^2/g)	Pore Volume (cm^3/g)	Pore Diameter (nm)	CO (mg) /gcat	Pt dispersion (%)
0.5% Pt/MCM-41	947	1.14	3.80	0.38	54
1% Pt/MCM-41	928	1.08	3.73	0.53	37
2% Pt/MCM-41	943	1.13	3.81	1.00	35
5% Pt/MCM-41	908	1.10	3.87	1.71	24

Table 2 Catalytic performance of Pt/MCM-41 for selective catalytic reduction of NO with C_3H_6 at different temperatures

Catalyst	Temp. (°C)	NO Conv. (%)	NO Conv. to N_2 (%)	NO Conv. to N_2O (%)	TOF/10^{-3} (s^{-1})	C_3H_6 Conv. (%)
0.5% Pt/MCM-41	200	2.0	2.0	0	2.7	1
	225	6.0	3.0	3.0	8.1	3.1
	250	17.0	6.2	10.8	23	11.7
	275	54.0	18.7	35.3	73	100
	300	37.0	8.5	28.5	50	100
1.0% Pt/MCM-41	200	4.0	2.2	1.8	3.9	4.0
	225	8.0	4.4	3.6	7.9	10.2
	250	61.0	16.9	44.1	60	100
	275	49.0	15.2	33.8	48	100
	300	36.0	11.6	24.4	35	100
2.0% Pt/MCM-41	200	13.0	7.2	5.8	6.8	14.5
	225	33.0	13.8	19.2	17	27.0
	250	59.0	15.2	43.8	31	100
	275	48.0	13.0	35.0	25	100
	300	37.0	10.0	27.0	19	100
5.0% Pt/MCM-41	200	7.0	1.3	5.7	2.1	3.3
	225	20.0	6.7	13.3	6.1	13.2
	250	63.6	15.4	48.2	19	100
	275	61.0	13.2	47.8	18	100
	300	47.0	10.6	36.4	14	100

Conditions: 0.1 g of catalyst, NO = 1000 ppm, C_3H_6 = 1000 ppm, O_2 = 2%, He = balance, total flow rate = 250 ml/min.

TOF (turnover frequency) is defined as the number of NO molecules converted per surface Pt atom per second.

Table 3 Main characteristics of the catalysts

Sample	BET Specific Surface Area (m^2/g)	Pore Volume (cm^3/g)	Pore Diameter (nm)	H_2/Cu (TPR) (mol/mol)	
				1st peak	2nd peak
Al-MCM-41	917	1.05	4.3	—	—
Ce-Al-MCM-41	904	1.09	4.2	—	—
Cu-Al-MCM-41	885	1.03	4.1	0.41	0.51
Ce-Cu-Al-MCM-41	871	1.03	4.8	0.36	0.49

Figure captions

Fig. 1 XRD patterns of the Pt/MCM-41 catalysts.

Fig.2 The effect of O_2 concentration on SCR activity on 1% Pt/MCM-41 catalyst. Reaction conditions: reaction temperature = 250 °C, catalyst = 0.2 g, NO = 1000 ppm, C_3H_6 = 1000 ppm, O_2 = 0-7.8%, He = balance, total flow rate = 250 ml/min. (Conversion of ( ) C_3H_6, ( ) NO, ( ) NO to N_2 and ( ) NO to N_2O.)

Fig. 3 The effect of temperature on SCR activity on 1% Pt/MCM-41 catalyst. Reaction conditions: catalyst = 0.2 g, NO = 1000 ppm, CH_4 = 3000 ppm, O_2 = 2%, He = balance, total flow rate = 250 ml/min. (Conversion of ( ) CH_4 and ( ) NO.)

Fig. 4 The effect of temperature on SCR activity on 1% Pt/MCM-41 catalyst. Reaction conditions: catalyst = 0.2 g, NO = 1000 ppm, C_2H_4 = 1500 ppm, O_2 = 2%, He = balance, total flow rate = 250 ml/min. (Conversion of ( ) C_2H_4, ( ) NO, ( ) NO to N_2 and ( ) NO to N_2O.)

Fig. 5 The effect of temperature on SCR activity on 1% Pt/MCM-41 catalyst. Reaction conditions: catalyst = 0.2 g, NO = 1000 ppm, C_3H_8 = 1000 ppm, O_2 = 2%, He = balance, total flow rate = 250 ml/min. (Conversion of ( ) C_3H_8, ( ) NO, ( ) NO to N_2 and ( ) NO to N_2O.)

Fig. 6 The effect of temperature on SCR activity on 1% Pt/MCM-41 catalyst. Reaction conditions: catalyst = 0.2 g, NO = 1000 ppm, C_3H_6 = 1000 ppm, O_2 = 2%, He = balance, total flow rate = 250 ml/min. (Conversion of ( ) C_3H_6, ( ) NO, ( ) NO to N_2 and ( ) NO to N_2O.)

Fig. 7 The effect of reaction time on SCR activity on 1% Pt/MCM-41 catalyst (a) in the absence of H_2O and SO_2 and (b) in the presence of H_2O and SO_2. Reaction conditions: reaction temperature = 225 °C, catalyst = 0.2 g, NO = 1000 ppm, C_3H_6 = 1000 ppm, O_2 = 2%, H_2O steam = 0 or 5%, SO_2 = 0 or 500 ppm, He = balance, total flow rate = 250 ml/min. (Conversion of ( ) C_3H_6, ( ) NO, ( ) NO to N_2 and ( ) NO to N_2O.)

Fig.8 XRD patterns of (a) Al-MCM-41, (b) Cu-Al-MCM-41, (c) Ce-Al-MCM-41, and (d) Ce-Cu-Al-MCM-41.

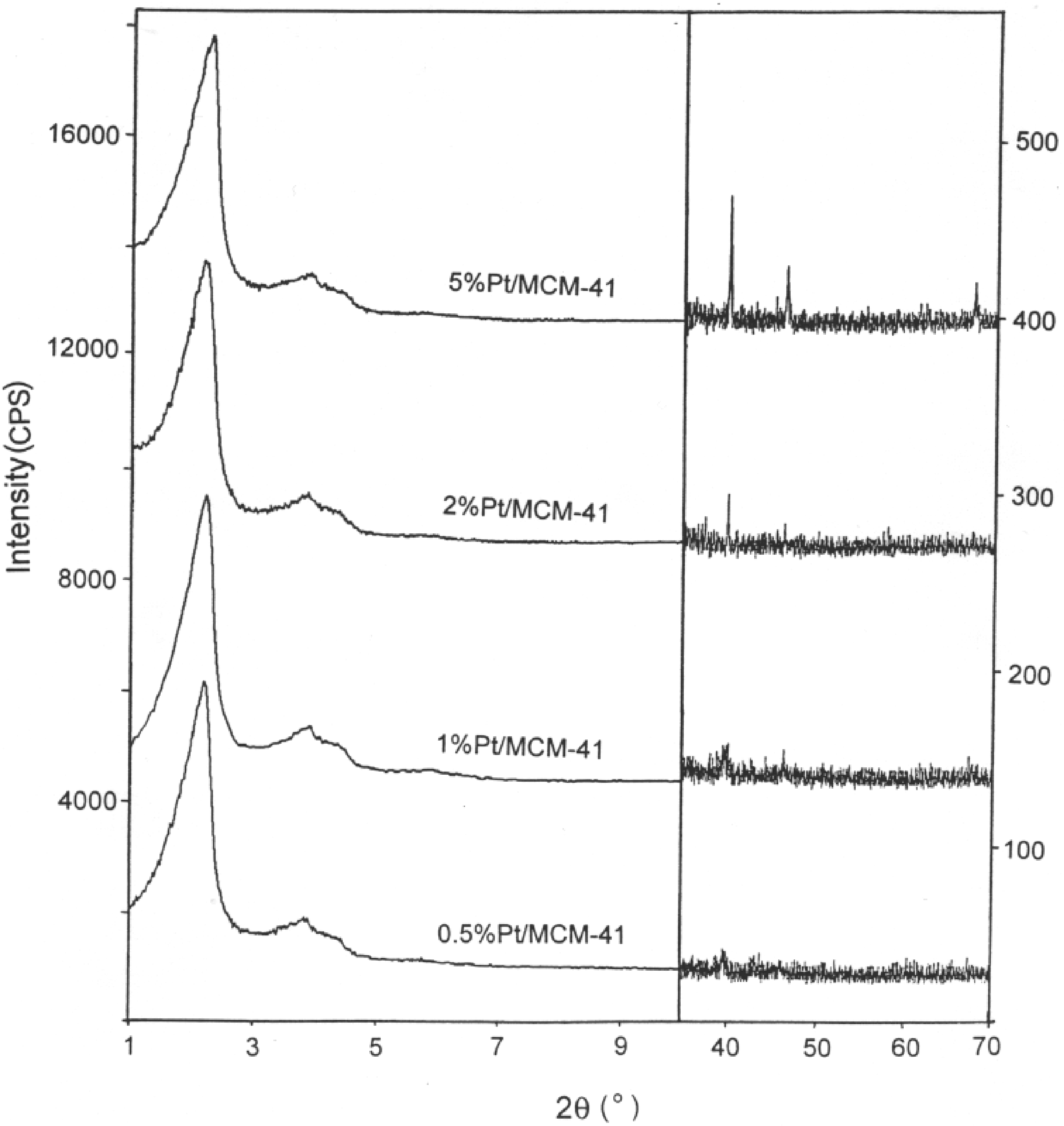
Fig. 9 TPR profiles of (a) Ce-Al-MCM-41, (b) Cu-Al-MCM-41 and (c) Ce-Cu-Al-MCM-41.

Fig.10 Conversions of NO_x for SCR reaction on (a) Ce-Al-MCM-41, (b) Cu-Al-MCM-41, (c) Ce-Cu-Al-MCM-41 and (d) Cu-ZSM-5 (data obtained from reference 11). Reaction conditions: catalyst = 0.5 g, [NO] = [C_2H_4] = 1000 ppm, [O_2] = 2%, He = balance, total flow rate = 250 ml/min, and space velocity ≈ 7500 h^{-1} .

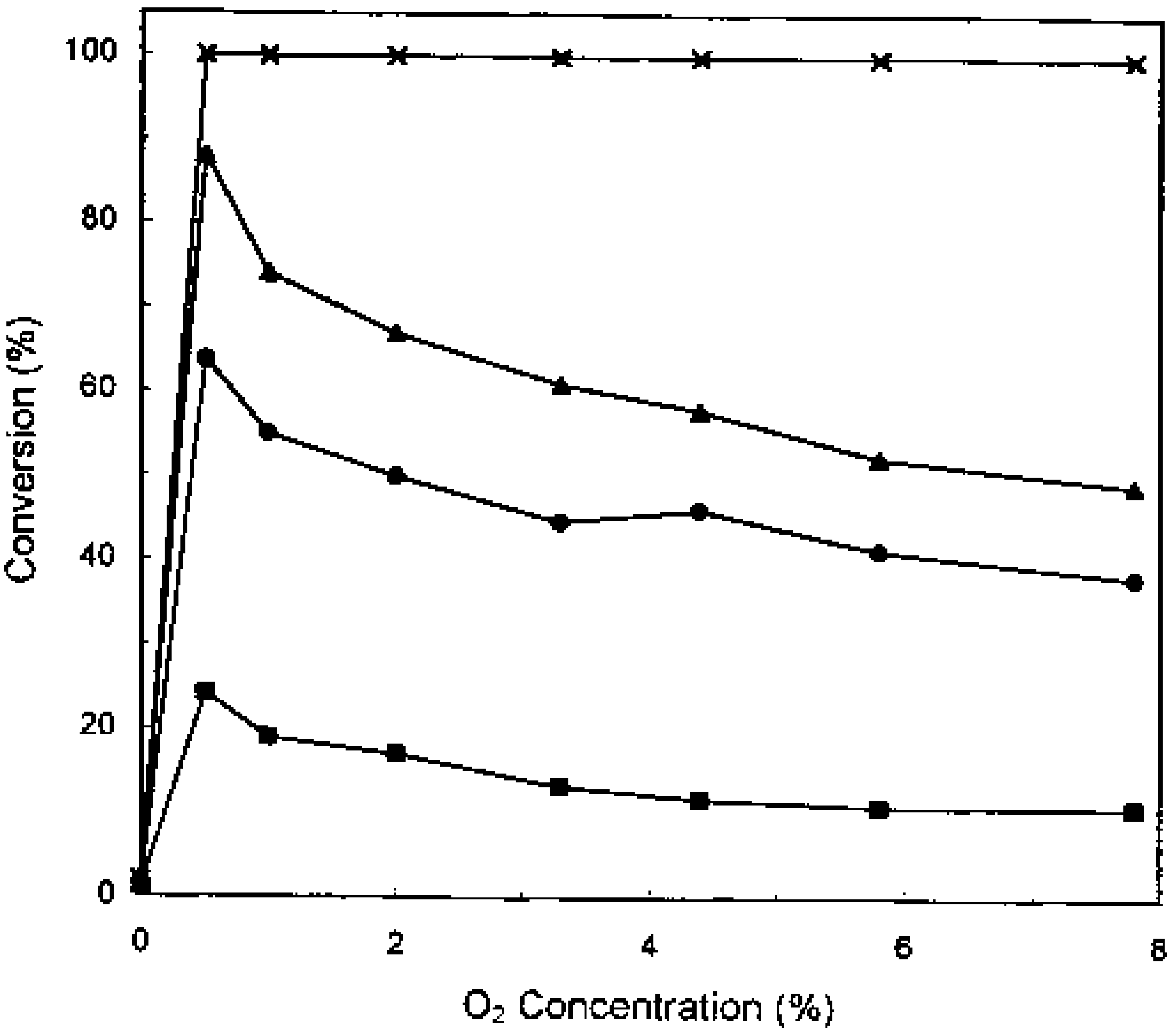
Fig.11 Conversions of C_2H_4 for SCR reaction on (a) Ce-Al-MCM-41, (b) Cu-Al-MCM-41 and (c) Ce-Cu-Al-MCM-41. Reaction conditions are the same as in Fig. 3.

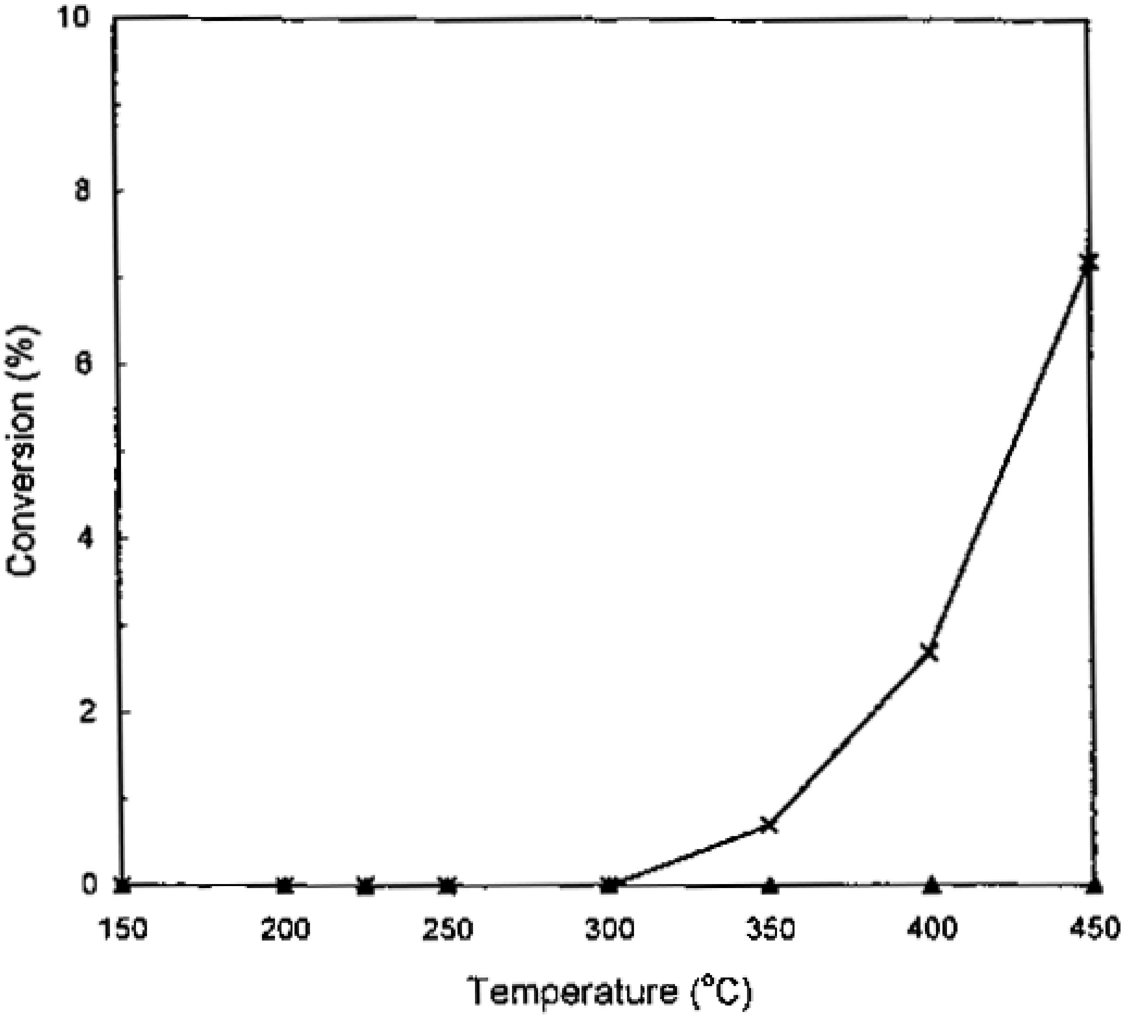
Fig. 12 Effect of O_2 concentration on SCR activity on Ce-Cu-Al-MCM-41 catalyst. Reaction conditions: temperature = 500 °C, catalyst = 0.5 g, [NO] = [C_2H_4] = 1000 ppm, He = balance, total flow rate = 250 ml/min, and space velocity ≈ 7500 h^{-1} .

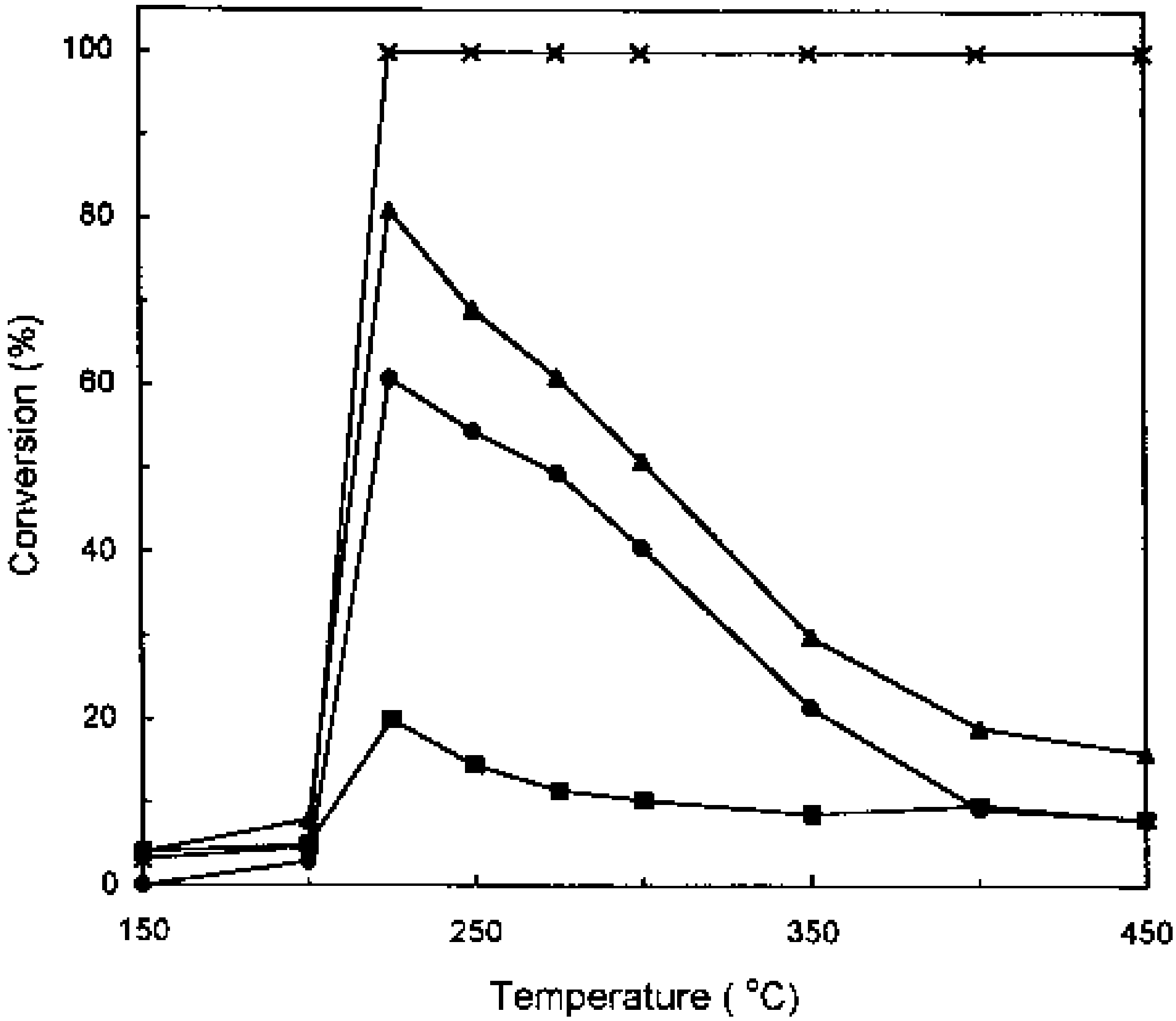
Fig. 13 Effect of H_2O and SO_2 on SCR activity over the Ce-Cu-Al-MCM-41 catalyst. Reaction conditions: temperature = 500 °C, catalyst = 0.5 g, [NO] = [C_2H_4] = 1000 ppm, [H_2O] = 2.3% (when used), [SO_2] = 500 ppm (when used), He = balance, total flow rate = 250 ml/min, and space velocity ≈ 7500 h^{-1} .



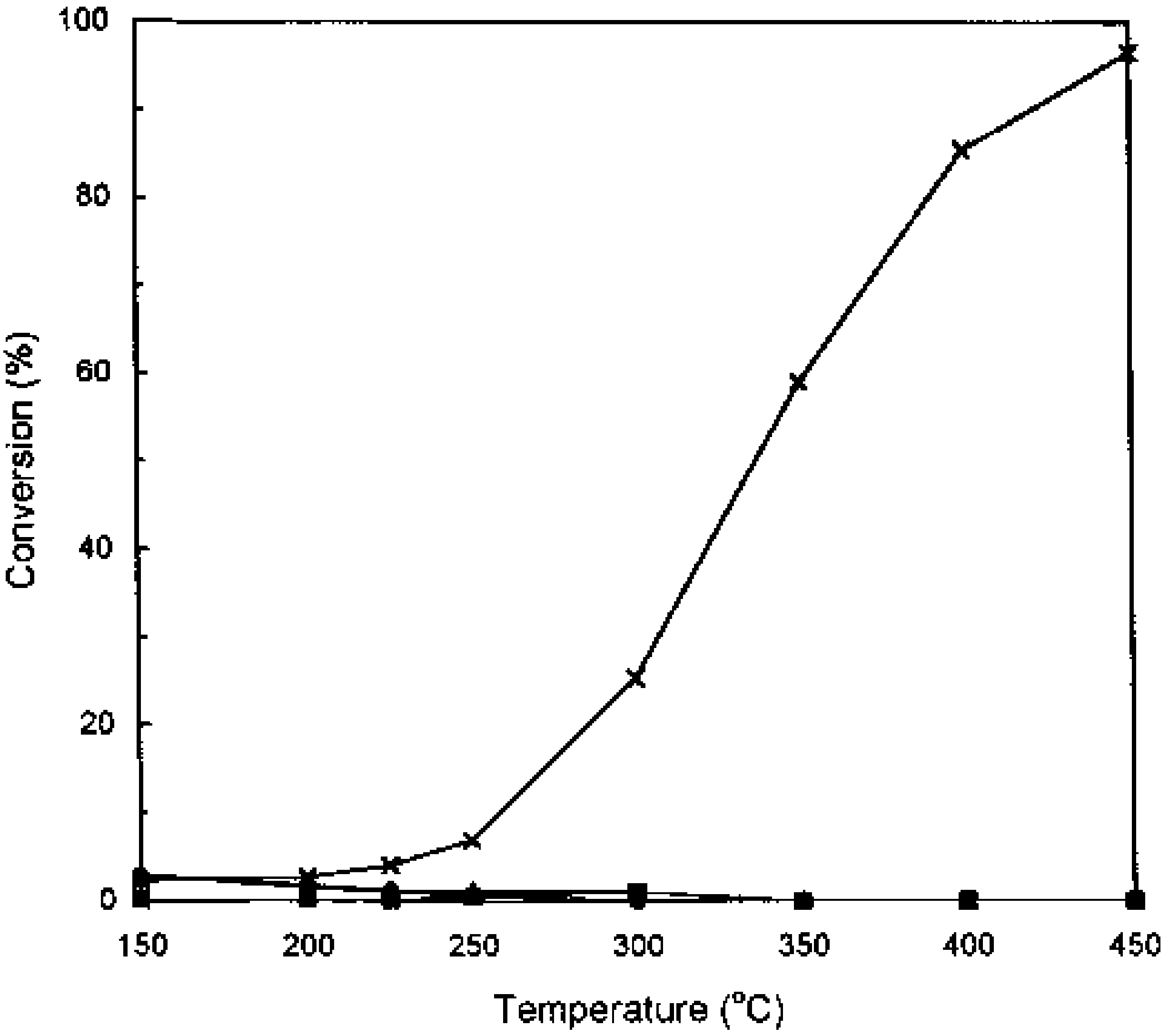
Intensity(CPS)
16000
12000
8000
4000
500
400
300
200
100
5%Pt/MCM-41
2%Pt/MCM-41
1%Pt/MCM-41
0.5%Pt/MCM-41
1
3
5
7
9
40
50
60
70
2θ (°)


Conversion (%)
0
20
40
60
80
100
0
2
4
6
8
O_2 Concentration (%)

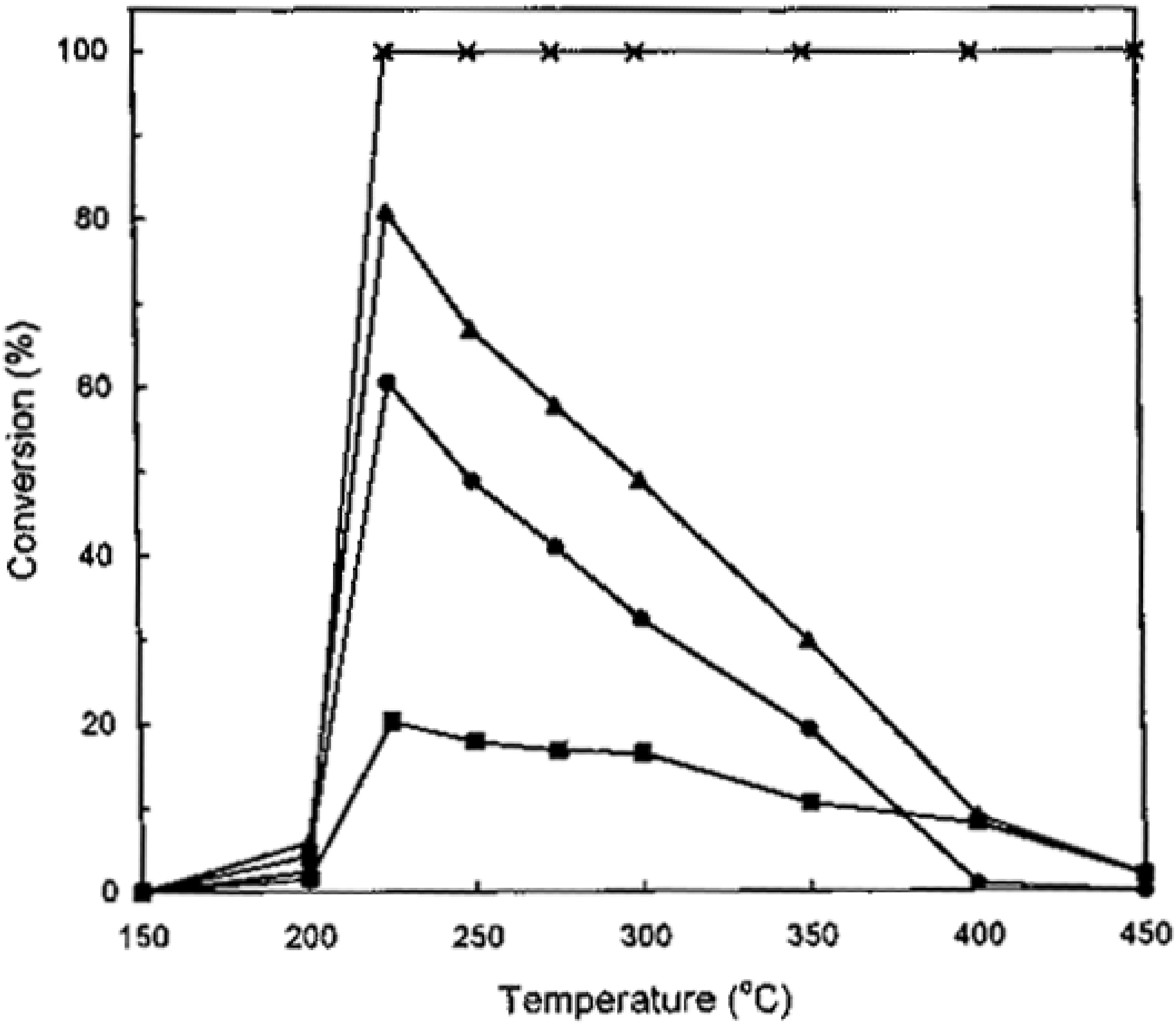

10
8
6
4
2
0
Conversion (%)
150
200
250
300
350
400
450
Temperature (°C)



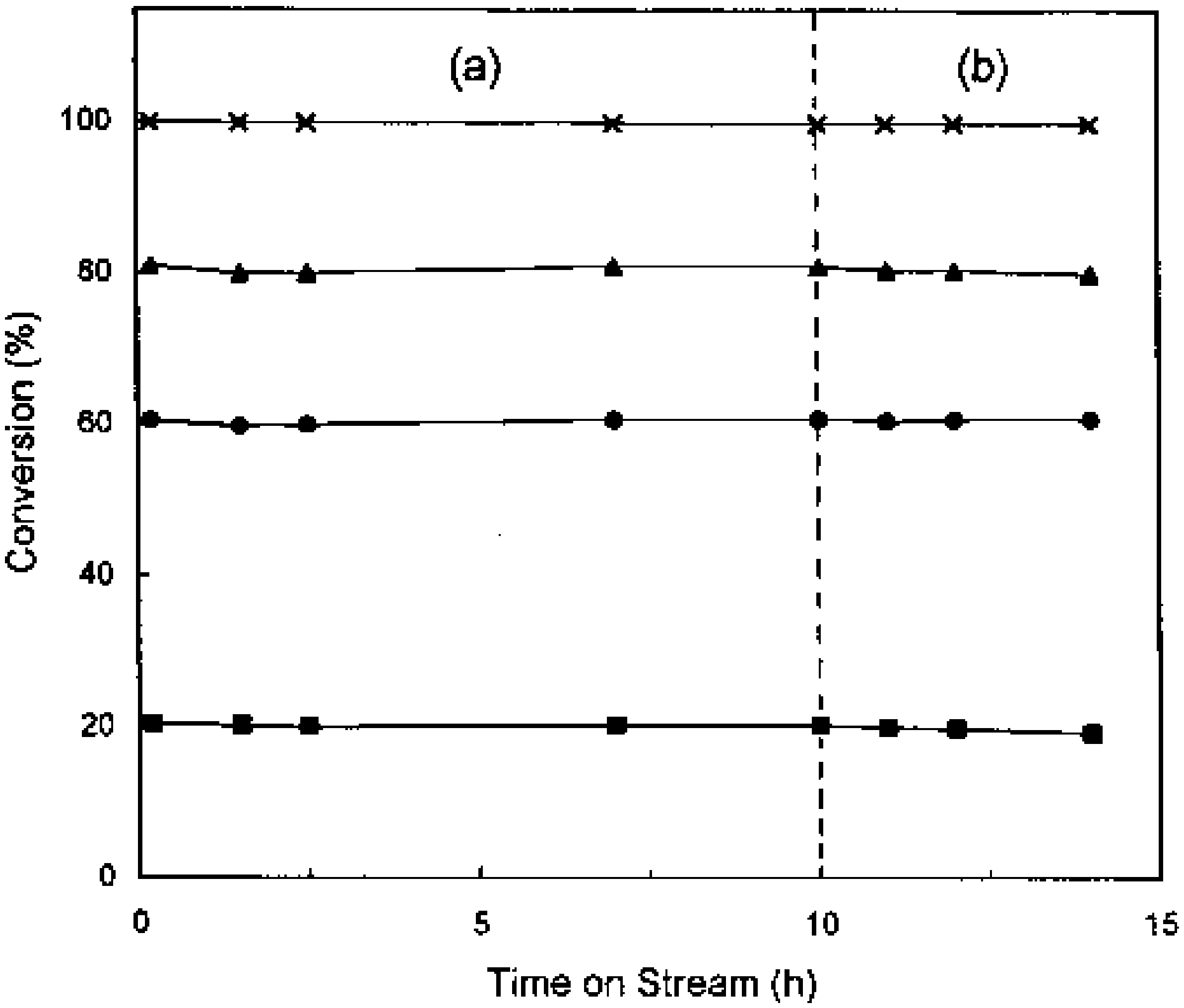
100
80
60
40
20
0
Conversion (%)
150
250
350
450
Temperature (°C)

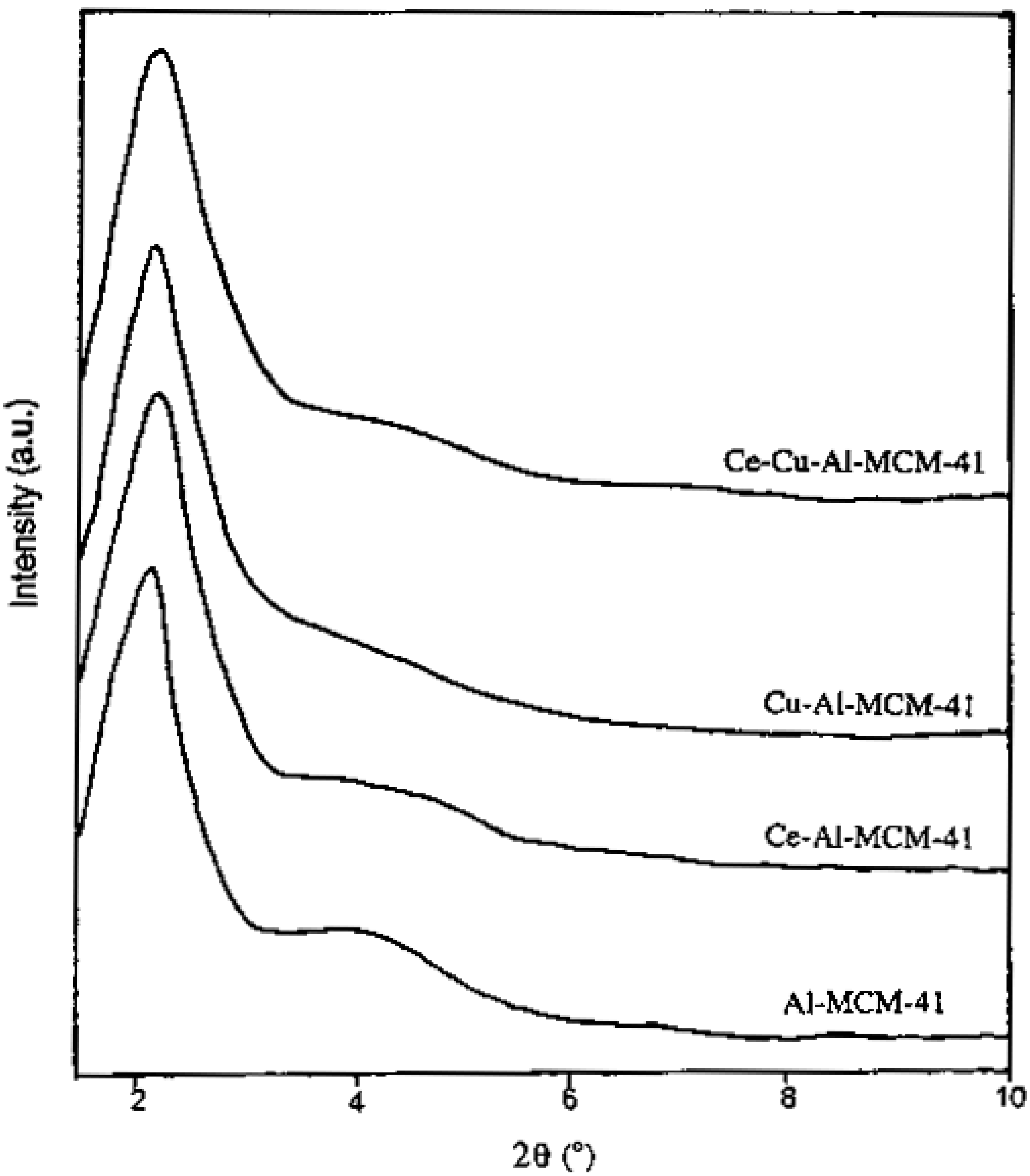


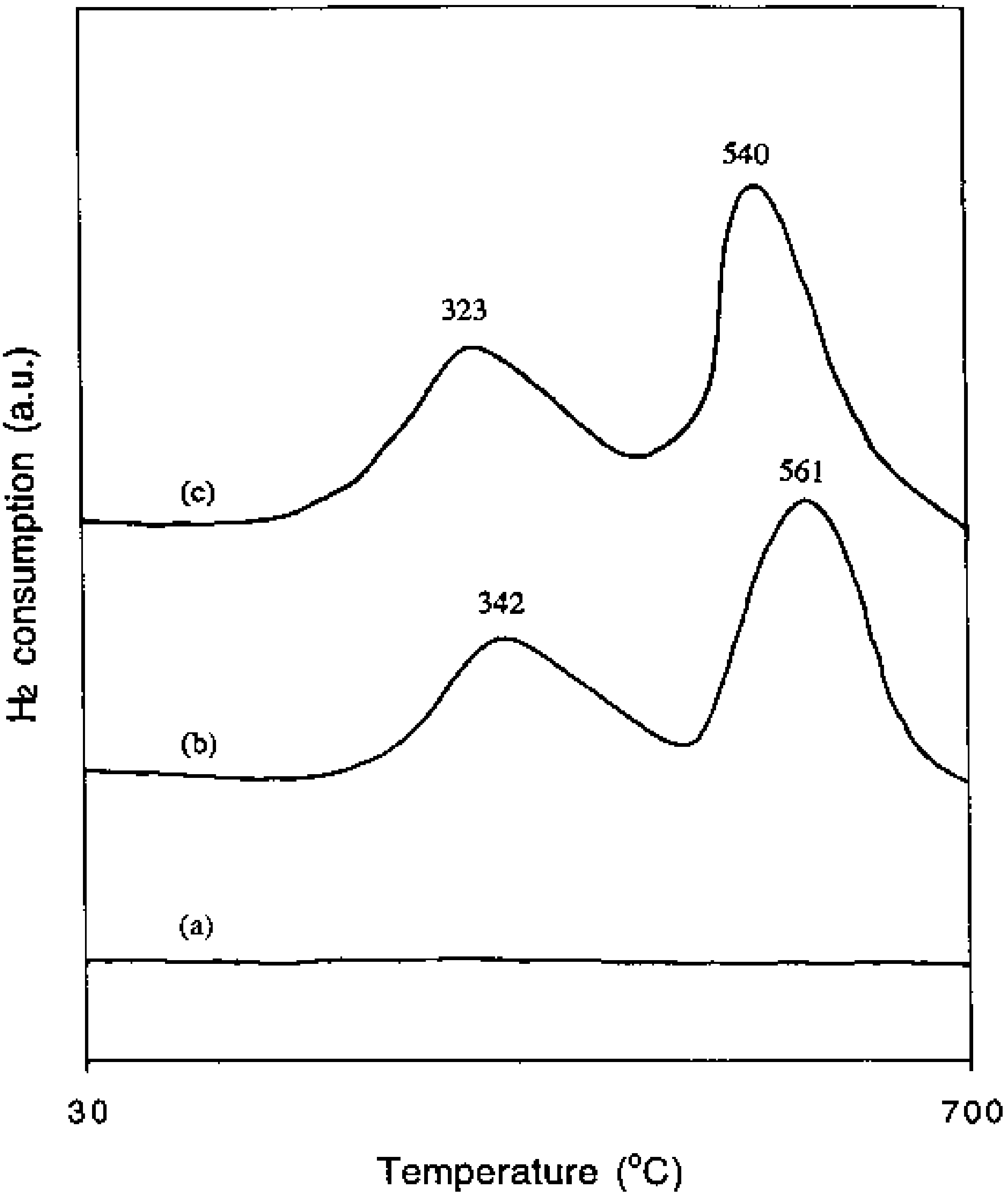
100
80
60
40
20
0
Conversion (%)
150
200
250
300
350
400
450
Temperature (°C)

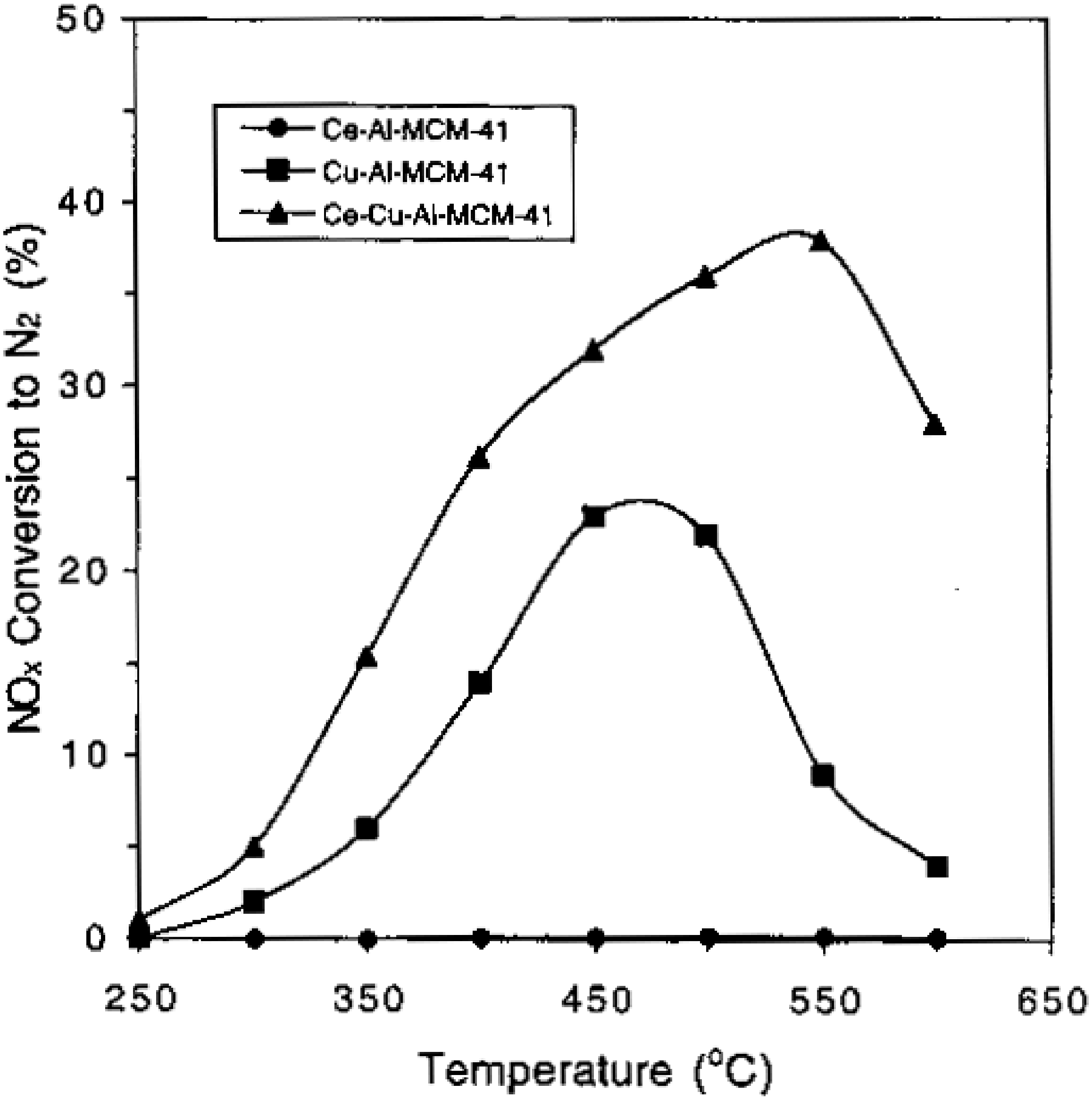


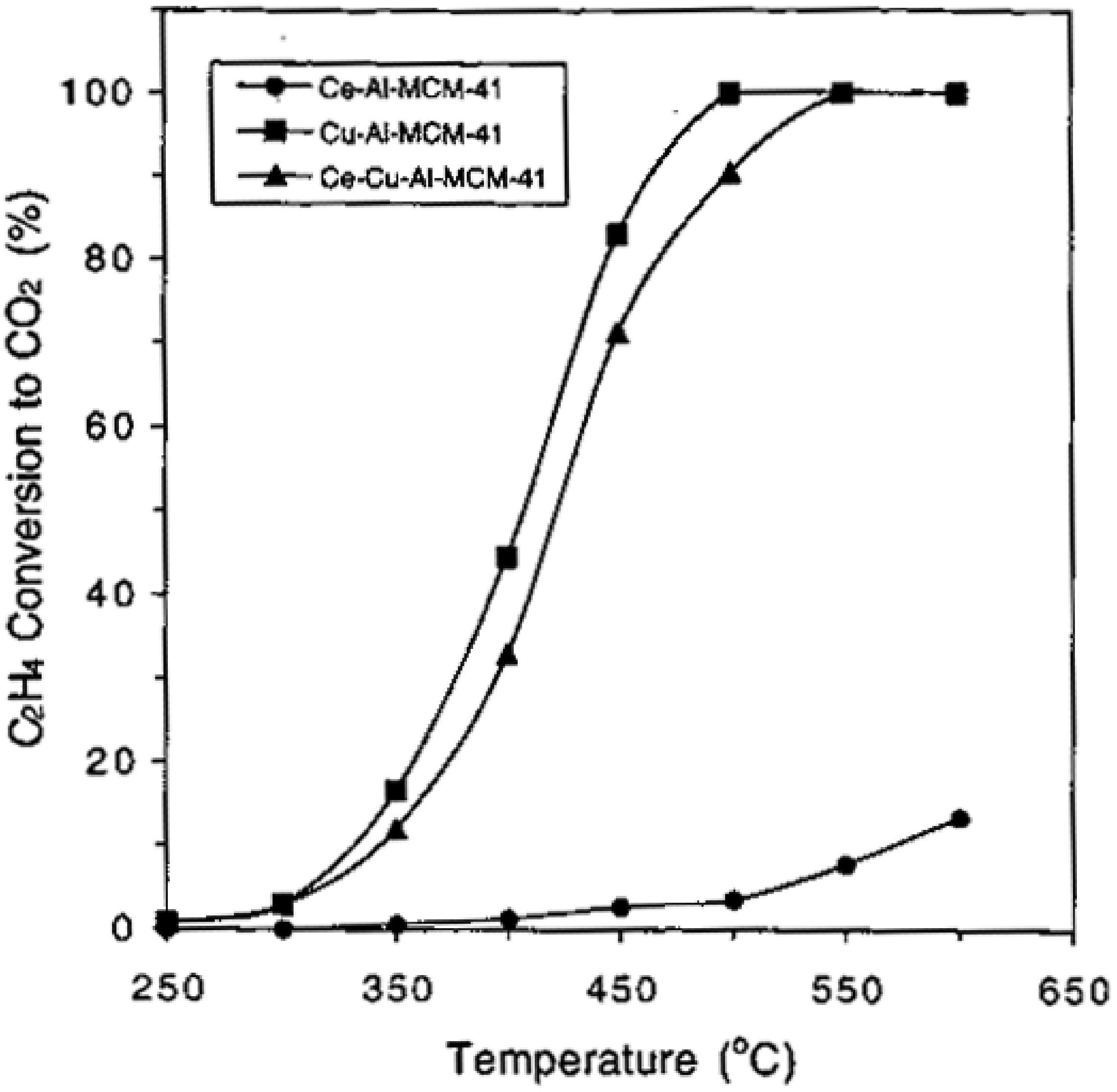
100
80
60
40
20
0
Conversion (%)
150
200
250
300
350
400
450
Temperature (°C)

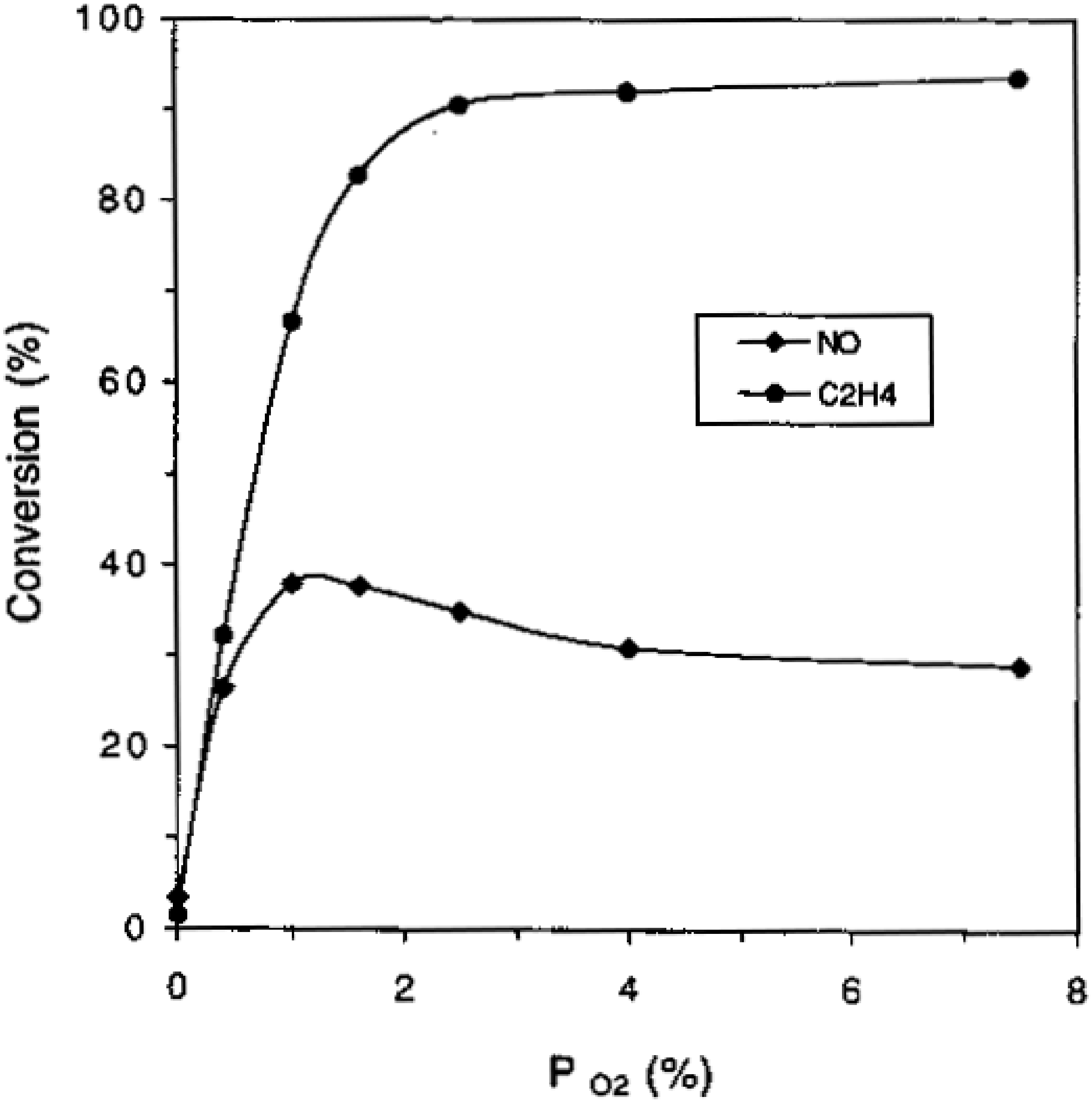

(a)
(b)
Conversion (%)
100
80
60
40
20
0
0
5
10
15
Time on Stream (h)


Intensity (a.u.)
Ce-Cu-Al-MCM-41
Cu-Al-MCM-41
Ce-Al-MCM-41
Al-MCM-41
2
4
6
8
10
2θ (°)

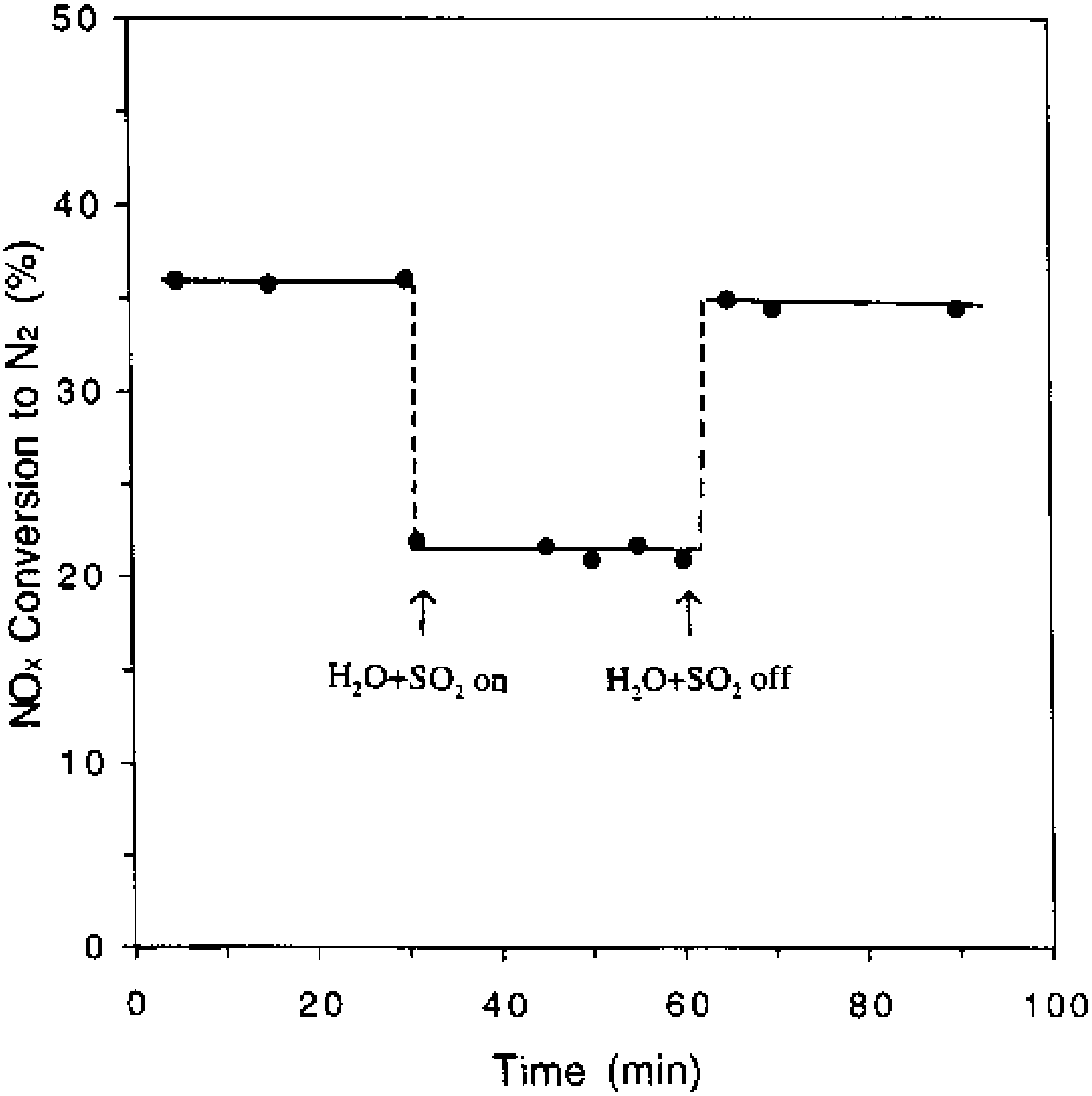

H₂ consumption (a.u.)
Temperature (°C)
30
700
(a)
(b)
(c)
342
561
323
540


50
40
30
20
10
0
250
350
450
550
650
NOx Conversion to N2 (%)
Temperature (°C)
Ce-Al-MCM-41
Cu-Al-MCM-41
Ce-Cu-Al-MCM-41


Ce-Al-MCM-41
Cu-Al-MCM-41
Ce-Cu-Al-MCM-41
C_2H_4 Conversion to CO_2 (%)
0
20
40
60
80
100
250
350
450
550
650
Temperature (°C)



100
80
60
40
20
0
Conversion (%)
0
2
4
6
8
P O2 (%)
NO
C2H4


50
40
30
20
10
0
NOx Conversion to N2 (%)
H2O+SO2 on
H2O+SO2 off
0
20
40
60
80
100
Time (min)