

Pt/MCM-41 catalyst for selective catalytic reduction of nitric oxide with hydrocarbons in the presence of excess oxygen

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First results are reported on the use of MCM-41 mesoporous molecular sieve as the support for Pt for the selective catalytic reduction of NO by hydrocarbons in the presence of O₂. MCM-41 provided the highest specific NO reduction rates for Pt as compared with all other supports reported in the literature, i.e., Al₂O₃, SiO₂ and ZSM-5.

Keywords: MCM-41, Pt supported on MCM-41, nitric oxide decomposition, SCR with hydrocarbon

1. Introduction

Removal of NO_x (NO + NO₂) from exhaust gases is a challenging subject that 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, V₂O₅/TiO₂ has been the main commercial catalyst for SCR with NH₃ for stationary sources [1]. However, for diesel- and gasoline-fueled engines in vehicles, the use of NH₃-based SCR technologies is not practical because of the high cost and NH₃ handling problems. The three-way catalyst has been used commercially in gasoline engines for reduction NO to N₂ 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], Cu²⁺-exchanged pillared clay [12,13], Fe-ZSM-5 [14], Pt-ZSM-5 [15–17], Rh-ZSM-5 [17], Pt/Al₂O₃ [18–20], and supported Ag [21]. Although Cu-ZSM-5 is very active and the most intensively studied catalyst, it suffers from severe deactivation in engine tests, mainly due to H₂O and SO₂ [22,23]. By comparison, Pt-ZSM-5 was found to be more active than Cu-ZSM-5 and Fe-MOR at lower temperatures (127–277 °C) [15], and the catalysts containing Pt were stable in real diesel exhaust [24]. They appeared to be some of the most promising catalysts.

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 [25,26]. Because it has

high thermal stability, high BET surface areas and large pore volumes, MCM-41 has already attracted considerable interest in recent years [27]. It has been studied as catalyst, support and sorbent [27]. Corma and co-workers [28] reported a good catalytic activity for MCM-41 in selective oxidation of hex-1-ene with H₂O₂, and norbornene with tert-butylhydroperoxide on Ti-MCM-41 catalyst. Fe–Al-MCM-41 was also reported by Yang et al. [29] as a good catalyst for selective catalytic reduction of NO with NH₃. In this work, we investigated the activity of platinum-doped MCM-41 in SCR of NO with methane, ethylene, propane and propylene in the presence of excess oxygen. The effects of oxygen, water vapor and sulfur dioxide on SCR activity were also studied.

2. Experimental

Pure-silica MCM-41 was synthesized according to the procedure given by Kim et al. [30]. 30.1 ml sodium silicate solution (containing 14% of NaOH and 27% of SiO₂, 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% NH₃ aqueous solution (J.T. Baker) and deionized water, with constant stirring at room temperature. The resulting gel mixture had the following molar composition: 1 SiO₂ : 0.166 CTMACl : 0.388 Na₂O : 0.0247 NH₄OH : 40 H₂O. 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 2 N HNO₃. 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 duration) 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

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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.

The powder X-ray diffraction (XRD) measurement was carried out with a Rigaku Rotaflex D/Max-C system with Cu K α ($\lambda = 0.1543$ nm) radiation. The samples were loaded on a sample holder with a depth of 1 mm. XRD patterns were recorded in the ranges of $2\theta = 1\text{--}10^\circ$ and $30\text{--}70^\circ$. 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 ($P/P_0 = 0.05\text{--}0.20$). 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 [31], 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 cooling 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 ratio for Pt $_s$:CO, Pt dispersions were obtained.

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. 0.1 or 0.2 g of sample was used in this work. The typical reactant gas composition was as follows: 1000 ppm NO, 1000–3000 ppm hydrocarbons (CH $_4$, C $_2$ H $_4$, C $_3$ H $_8$ and C $_3$ H $_6$), 0–7.8% O $_2$, 500 ppm SO $_2$ (when used), 2.4% 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 $_2$ H $_4$ in He, 1.07% C $_3$ H $_6$ in He, 0.98% C $_3$ H $_8$ 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 $_2$ O, C $_2$ H $_4$, C $_3$ H $_6$ and C $_3$ H $_8$. Other details of the SCR reaction system were described elsewhere [32].

3. Results and discussion

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 $2\theta = 3.77$, 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 [25,26,30]. 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 (figure 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 $_3$ H $_6$ is shown in table 2. At lower temperatures (below 200 °C), NO conversion and C $_3$ H $_6$ 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 propylene conversion reached 100%. Carbon dioxide was the only product (beside water) of propylene 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 $_2$ O was the main product. This may be related to the fact that platinum is a poor N $_2$ O decomposition catalyst [20,33]. When the platinum amount increased from 0.5 to 5%, the peak NO conversion temperature decreased from 275 to 250 °C. At high temperatures, the decrease in NO conversion was due to the oxidation of C $_3$ H $_6$ 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]

$$\text{NO reduction rate} = -d[\text{NO}]/dt = F_0 X/w, \quad (1)$$

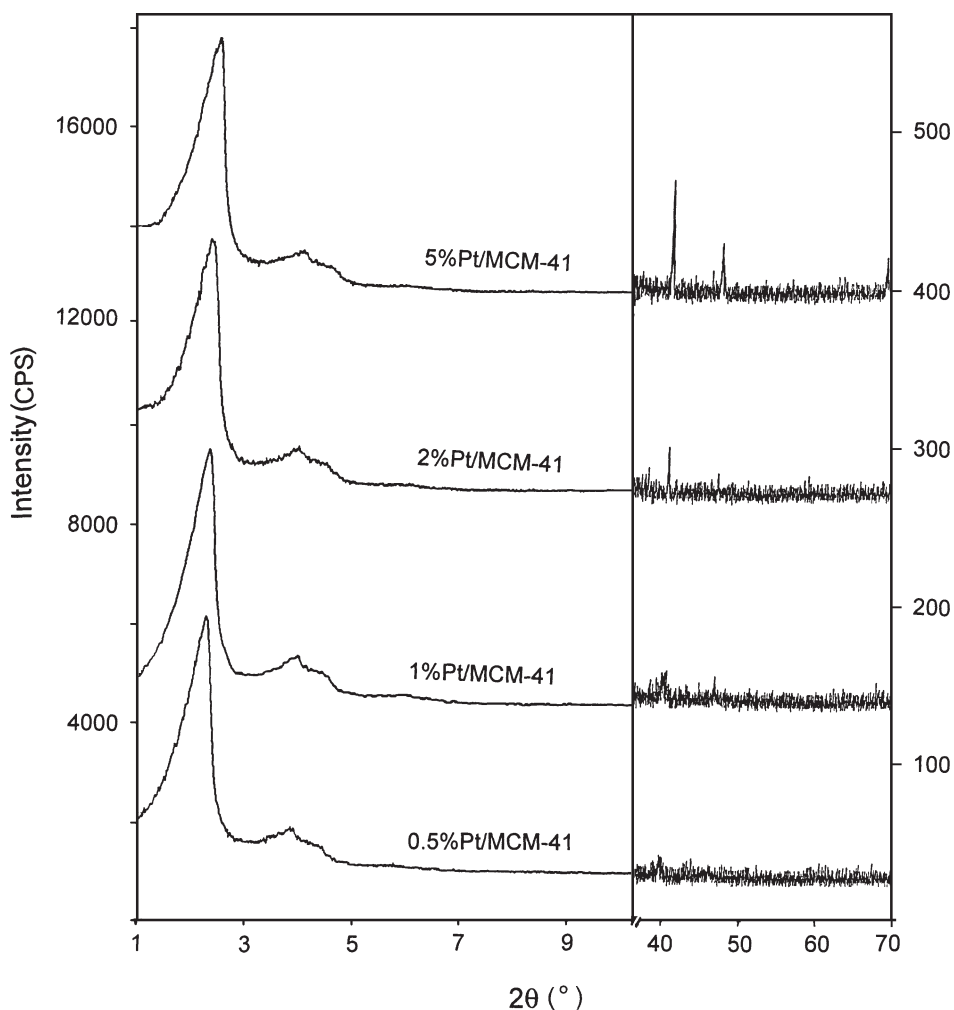


Figure 1. XRD patterns of the Pt/MCM-41 catalysts.

Table 1
Platinum 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/g-cat)	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

where F_0 is inlet molar flow rate of NO, X is NO conversion, and w is weight of the catalyst. The maximum NO reduction rates 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/Al₂O₃ catalyst [20] under similar conditions. Hamada et al. [18] 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 [15,17]. It was claimed that Pt was ion-exchanged on ZSM-5 [15,17]. However, characterization of these materials has indicated that in many cases Pt exists on the exterior surface of the ZSM-5 crystals as fine metallic particles, 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 [29].

It is well known that oxygen is important in SCR reactions of NO both by hydrocarbons [34] and by NH₃ [1]. The effect of O₂ on SCR by C₃H₆ over 1% Pt/MCM-41 at 250 °C was studied, and the results are shown in figure 2. In the absence of O₂, almost no activity was obtained. When 0.5% of O₂ was added to the reactant gas mixture, NO conversion was found to increase significantly to 88%, and C₃H₆ conversion also reached 100% at the

Table 2
Catalytic performance of Pt/MCM-41 for selective catalytic reduction of NO with C₃H₆ at different temperatures.^a

Catalyst	Temp. (°C)	NO conv. (%)	NO conv. to N ₂ (%)	NO conv. to N ₂ O (%)	TOF ^b /10 ⁻³ (s ⁻¹)	C ₃ H 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

^a Conditions: 0.1 g of catalyst, NO = 1000 ppm, C₃H₆ = 1000 ppm, O₂ = 2%, He = balance, total flow rate = 250 ml/min.

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

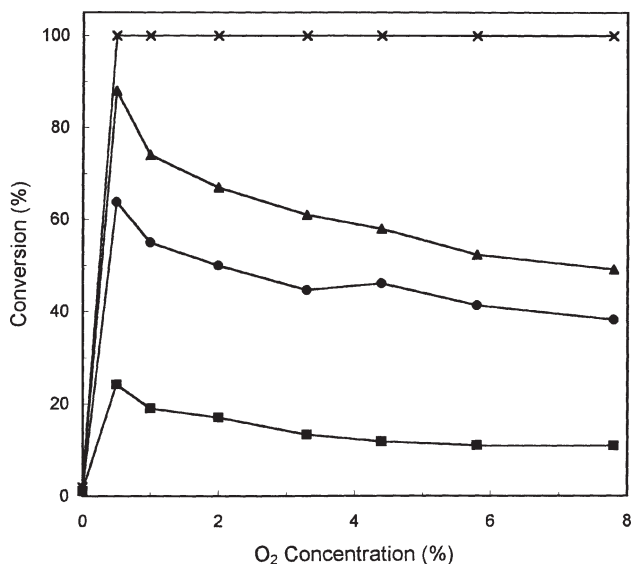


Figure 2. The effect of O₂ concentration on SCR activity on 1% Pt/MCM-41 catalyst. Reaction conditions: reaction temperature = 250 °C, catalyst = 0.2 g, NO = 1000 ppm, C₃H₆ = 1000 ppm, O₂ = 0–7.8%, He = balance, total flow rate = 250 ml/min. (Conversion of (×) C₃H₆, (▲) NO, (■) NO to N₂ and (●) NO to N₂O.)

same temperature. After that, NO conversion decreased slightly with the increase of O₂ 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/Al₂O₃ catalyst surface were in the reduced form under the reaction conditions, and

that NO did not convert to N₂ on a completely oxidized, supported platinum catalyst [19,35]. In this work, after the Pt/MCM-41 catalysts were calcined at 500 °C in air (21% of O₂), 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 CH₄, C₂H₄ and C₃H₈ as reductants at the same carbon concentration condition, i.e., 3000 ppm of CH₄, 1500 ppm of C₂H₄ and 1000 ppm of C₃H₈, as compared with 1000 ppm of C₃H₆. The results are shown in figures 3–6. For CH₄ and C₃H₈, no or little activity for NO reduction was found on the 1% Pt/MCM-41 catalyst in the temperature range of 150–450 °C (figures 3 and 5). At higher temperatures, only a small amount of CH₄ was oxidized to CO₂ by O₂, while a large amount of C₃H₈ was converted to CO₂ by O₂. By comparison, a very high activity was obtained when C₂H₄ and C₃H₆ were used as the reductants (figures 4 and 6). The maximum NO conversion reached 81% at 225 °C. This indicated that C₂H₄ and C₃H₆ were excellent reductants but CH₄ and C₃H₈ were poor reductants for SCR of NO over the Pt/MCM-41 catalyst. Similar phenomenon was

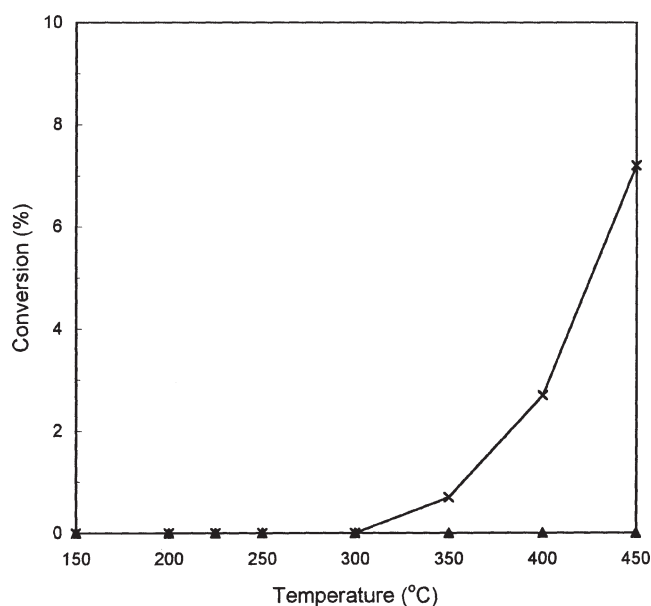


Figure 3. The effect of temperature on SCR activity on 1% Pt/MCM-41 catalyst. Reaction conditions: catalyst = 0.2 g, NO = 1000 ppm, CH₄ = 3000 ppm, O₂ = 2%, He = balance, total flow rate = 250 ml/min. (Conversion of (x) CH₄ and (▲) NO.)

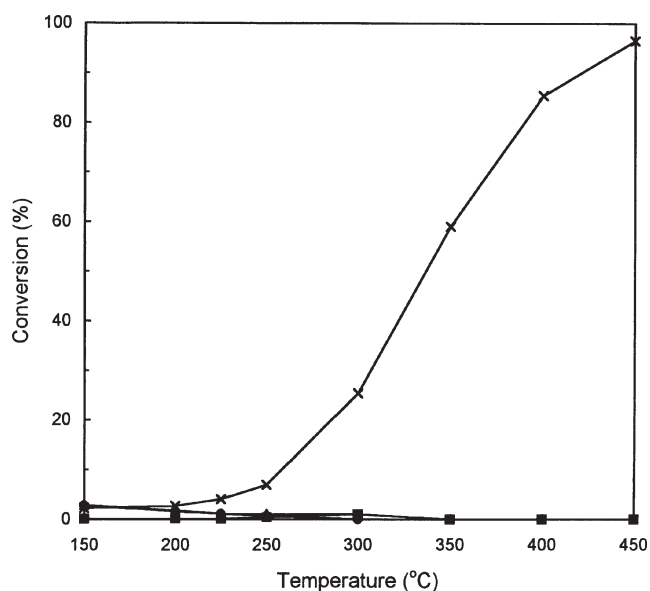


Figure 5. The effect of temperature on SCR activity on 1% Pt/MCM-41 catalyst. Reaction conditions: catalyst = 0.2 g, NO = 1000 ppm, C₃H₈ = 1000 ppm, O₂ = 2%, He = balance, total flow rate = 250 ml/min. (Conversion of (x) C₃H₈, (▲) NO, (■) NO to N₂ and (●) NO to N₂O.)

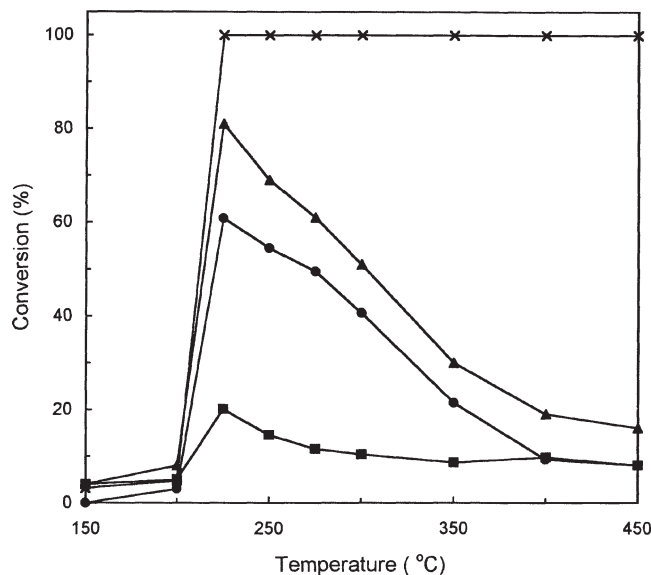


Figure 4. The effect of temperature on SCR activity on 1% Pt/MCM-41 catalyst. Reaction conditions: catalyst = 0.2 g, NO = 1000 ppm, C₂H₄ = 1500 ppm, O₂ = 2%, He = balance, total flow rate = 250 ml/min. (Conversion of (x) C₂H₄, (▲) NO, (■) NO to N₂ and (●) NO to N₂O.)

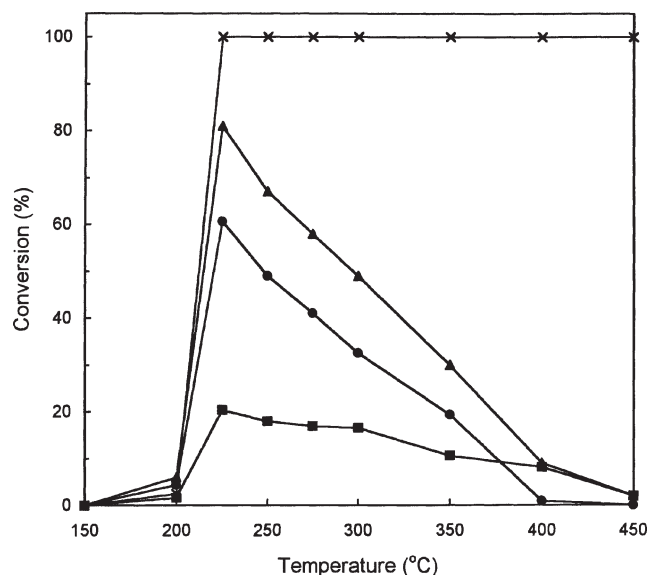


Figure 6. The effect of temperature on SCR activity on 1% Pt/MCM-41 catalyst. Reaction conditions: catalyst = 0.2 g, NO = 1000 ppm, C₃H₆ = 1000 ppm, O₂ = 2%, He = balance, total flow rate = 250 ml/min. (Conversion of (x) C₃H₆, (▲) NO, (■) NO to N₂ and (●) NO to N₂O.)

observed on Pt/Al₂O₃ and Pt/SiO₂ catalysts [36]. This difference is related to the nature of these hydrocarbons. Ethylene and propylene have a C=C double bond and are easy to adsorb on platinum atoms and thus result in a high coverage 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 CH₄ molecule (105 kcal/mol) is larger than that in C₃H₈ molecule (95 kcal/mol), a higher C₃H₈ conversion was obtained using C₃H₈ as the reductant than that using CH₄ 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. Ethylene and propylene are better reductants than methane and propane on the Pt/MCM-41 catalyst.

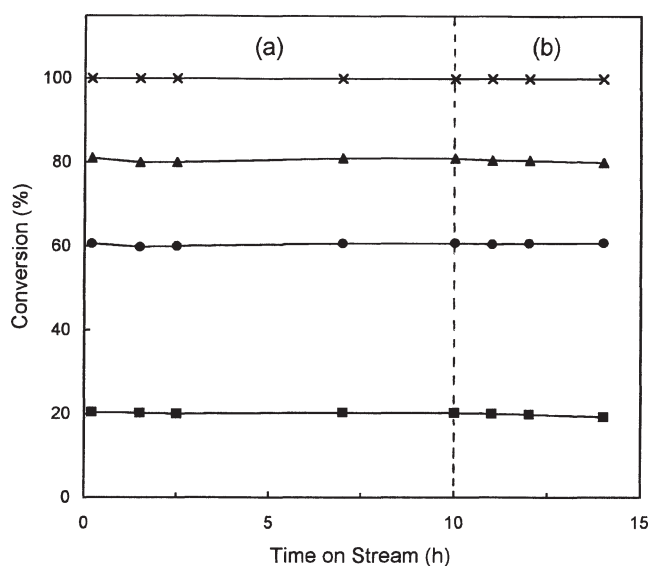


Figure 7. The effect of reaction time on SCR activity on 1% Pt/MCM-41 catalyst (a) in the absence of H₂O and SO₂, and (b) in the presence of H₂O and SO₂. Reaction conditions: reaction temperature = 225 °C, catalyst = 0.2 g, NO = 1000 ppm, C₃H₆ = 1000 ppm, O₂ = 2%, H₂O steam = 0 or 2.4%, SO₂ = 0 or 500 ppm, He = balance, total flow rate = 250 ml/min. (Conversion of (×) C₃H₆, (▲) NO, (■) NO to N₂ and (●) NO to N₂O.)

The effect of H₂O and SO₂ on SCR activity of NO with C₃H₆ on 1% Pt/MCM-41 catalyst is shown in figure 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 C₃H₆, 2% of O₂, He as balance and 250 ml/min of total flow rate, NO conversion remained at 80–81%. When 2.4% water vapor and 500 ppm SO₂ were added to the reactant gas, the catalytic performance remained unchanged in the following 4 h at 225 °C.

4. Conclusions

0.5–5 wt% Pt/MCM-41 catalysts were prepared and studied for the selective catalytic reduction of NO with CH₄, C₂H₄, C₃H₆ and C₃H₈ in the presence of excess oxygen. The catalysts had high BET surface areas (>900 m²/g) and large pore volumes (>1.00 cm³/g). Platinum metal particles were detected in these catalysts at room temperature by XRD. A high activity for NO reduction was obtained when C₂H₄ or C₃H₆ 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 C₃H₆, 2% of O₂ and He as balance; but no or little activity was found when CH₄ or C₃H₈ was used. This difference was related to the different nature of these hydrocarbons. The Pt/MCM-41 catalyst showed a good stability. H₂O and SO₂ did not cause deactivation of the catalyst.

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