Catalysis Letters 39 (1996) 269–274

Silica-supported cobalt catalysts for the selective reduction of nitrogen monoxide with propene

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Received 14 October 1995; accepted 5 March 1996

Catalytic behavior of silica-supported transition metals for NO reduction with propene in the presence of oxygen was investigated. While both silica and cobalt oxides did not show any activity for the selective NO reduction, impregnated CoO/SiO_2 prepared from cobalt acetate showed good activity although the preparation conditions had significant effect on the activity. It was suggested that highly dispersed surface Co^{2+} ions on silica are responsible for the catalytic activity.

Keywords: nitrogen monoxide; selective reduction; propene; transition metal; cobalt; silica

1. Introduction

The selective reduction of NO with hydrocarbons has been studied over various catalysts. Although most of the reports are related to zeolite type catalysts, activity of metal oxides has also been reported [1]. For single metal oxides, we reported that solid acid or base type oxides such as Al_2O_3, ZrO_2 and MgO showed catalytic activity for this reaction, while SiO_2 was inactive [2]. Fourth period transition metal oxides such as Co_3O_4, CuO and Fe_2O_3 do not catalyze NO reduction in oxidizing atmospheres but promote only hydrocarbon oxidation. We also reported, however, that supporting small amounts of these metals promotes the activity of alumina at lower temperatures [3,4], although preparation conditions affected the catalytic activity. Similar promoting effects were also observed for a number of metal oxide-based catalysts such as Ag/Al_2O_3 [5], Au/Al_2O_3 [6], $Cu/SiO_2–Al_2O_3$ [7] and V/TiO_2 [8]. Although the role of the supported metals has not been elucidated clearly, there seems to be a consensus that they promote NO reduction by catalyzing oxidation of NO to NO_2 or of the hydrocarbon to partially oxidized hydrocarbons. In any case, it is considered that the NO reduction activity results from cooperation between the supported metals and the support.

In this paper, we studied the catalytic behavior of some silica-supported 4th period transition metals and found that appropriate preparation procedures gave active catalysts for NO reduction with hydrocarbons in the presence of oxygen, although the silica support had no activity for NO reduction. This situation is somewhat different from that of the above-mentioned cases. Therefore, the catalytic active sites were investigated through various characterization techniques.

2. Experimental

The silica used in this study was supplied from Fuji-Davison Chemicals (Cariact-10, 310 $m^2\ g^{-1}$). Silica-supported transition metal catalysts were prepared by impregnating SiO_2 with aqueous metal salt solutions, followed by drying at 110°C and calcination under various conditions. The samples are abbreviated as x% MO (precursor salt)/SiO_2(calcination temperature in °C, atmosphere), where x is the metal loading as MO, and M is a metal element.

Catalytic activity was measured with a fixed bed flow reactor. The reaction gas contained NO (1000 ppm), O_2 (10%) and propene (1000 ppm) diluted in helium and the gas flow rate was 66 $cm^3\ min^{-1}$, unless otherwise specified. The catalysts were pretreated at 500°C for 1 h in helium. Then the reaction gas was fed to the catalyst bed. The reaction temperature was lowered stepwise after reaching steady-state at each temperature.

The effluent gas was analyzed by gas chromatography. A Molecular Sieve 5A column was used for the analysis of N_2 and CO and a Porapak Q column for the analysis of N_2O, CO_2 and hydrocarbons. The concentration of NOx (NO plus NO_2) in the effluent gas was always monitored by a chemiluminescence NOx analyzer. N_2, CO and CO_2 were the main products of the reaction. Small amounts of N_2O and ethene were also detected. However, their yields were less than a few percent. The carbon balance and the nitrogen balance were quite good although the latter sometimes dropped to 90% possibly because NO_2 formed could not easily reach the NOx analyzer. Therefore, the catalytic activity was expressed by the conversion of NO into N_2 and that of propene into COx (CO and CO_2).

For catalyst characterization, XRD, XPS, NO chemisorption and ammonia TPD measurements were made. The amount of chemisorbed NO was measured with a

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pulse method. The sample was first pretreated at 400°C in helium flow for 1 h and the temperature was cooled down to 50°C. Then pulses of NO were introduced onto the sample and the effluent gas was analyzed by TCD. The pulse was introduced until NO was not adsorbed any more. Ammonia TPD measurement was performed as follows. The sample in a quartz cell was first evacuated at 500°C and cooled down to 100°C. Then 100 Torr of ammonia was introduced into the cell and the adsorption was done for 1 h. After that, the gaseous ammonia was evacuated and the sample temperature was increased at a rate of 10°C/min. TCD was used to analyze the desorbed ammonia.

3. Results and discussion

3.1. Activity of silica-supported 4th period transition metals

The activity of several silica-supported 4th period transition metals prepared from metal acetate calcined in air at 500°C (MO(A)/SiO_2(500, air)) was investigated. The metal loading was fixed at 5 wt% as MO. As is shown in fig. 1, CoO/SiO_2 was the most active for NO reduction with the maximum NO conversion at 350°C. The activity of NiO/SiO_2 was lower than that of CoO/SiO_2. CuO and MnO/SiO_2 also gave lower NO conversion, although the maximum NO conversion was obtained at a temperature as low as 300°C. It is noted from the propene conversion data that the oxidation activity of CuO and MnO/SiO_2 is higher than that of CoO and NiO/SiO_2.

3.2. Catalytic behavior of CoO/SiO_2 catalysts

Since CoO/SiO_2 was the most active for NO reduction, the performance of CoO/SiO_2 catalysts was investigated further. Fig. 2 shows the catalytic activities of 5% CoO/SiO_2 prepared from various cobalt salt precursors, for which the final calcination was done in air at 500°C. CoO(N) and CoO(Cl)/SiO_2, which were prepared from cobalt nitrate and cobalt chloride respectively, were completely inactive for NO reduction, whereas CoO(A)/SiO_2 showed good activity. The former catalysts were, however, quite active for complete propene oxidation, CO_2 being the only product. On the other hand, CO was formed on CoO(A)/SiO_2 in addition to CO_2.

Fig. 3 presents the effect of cobalt loading on the activity of CoO(A)/SiO_2 calcined at 500°C in air. The NO reduction activity increased with cobalt loading up to 5%. However, 10% CoO(A)/SiO_2 gave lower NO conversions than those on 5% CoO(A)/SiO_2. Propene oxidation activity increased with cobalt loading up to 5%, but remained unchanged afterwards, namely, propene conversion to COx on 10% CoO(A)/SiO_2 was almost the same as that on 5% CoO(A)/SiO_2.

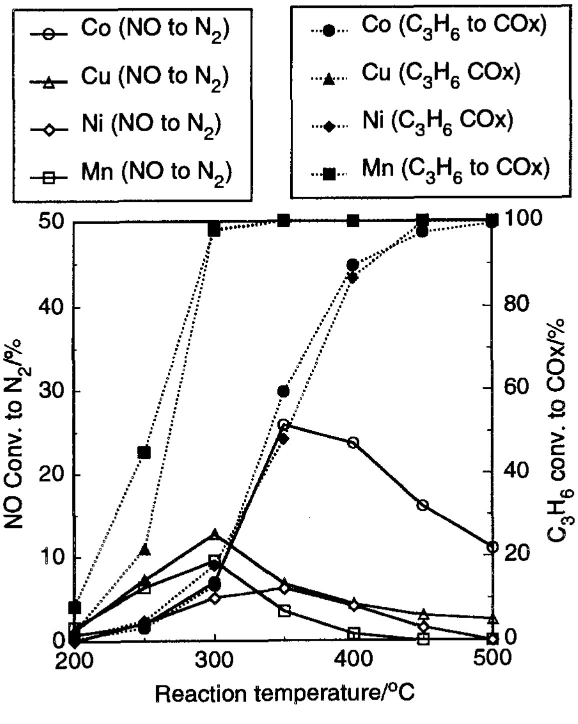

Fig. 1. Catalytic activities of impregnated 5% silica-supported transition metals prepared from metal acetate. Reaction conditions: NO = 1000 ppm, C_3H_6 = 1000 ppm, O_2 = 10%, W/F = 0.2 g s cm^{-3}.

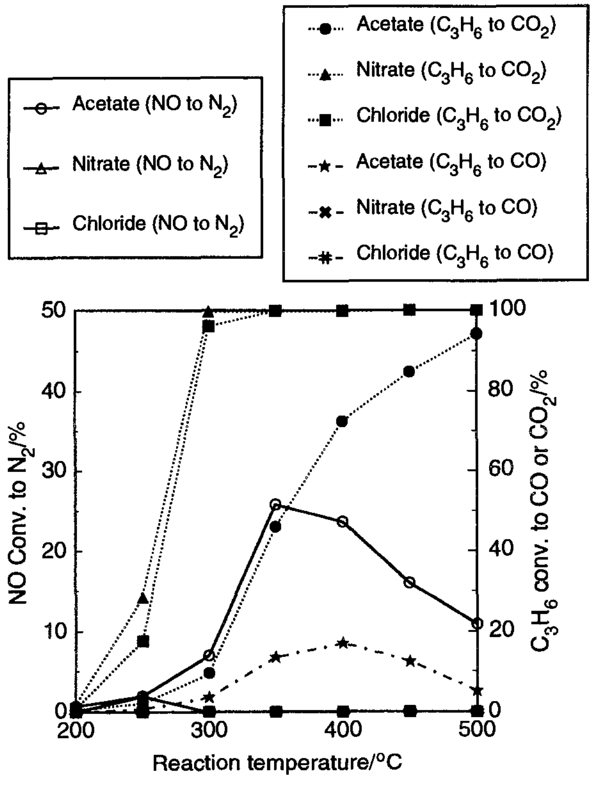

Fig. 2. Catalytic activities of 5% CoO/SiO_2 prepared from various cobalt precursors. Reactions conditions: NO = 1000 ppm, C_3H_6 = 1000 ppm, O_2 = 10%, W/F = 0.2 g s cm^{-3}.

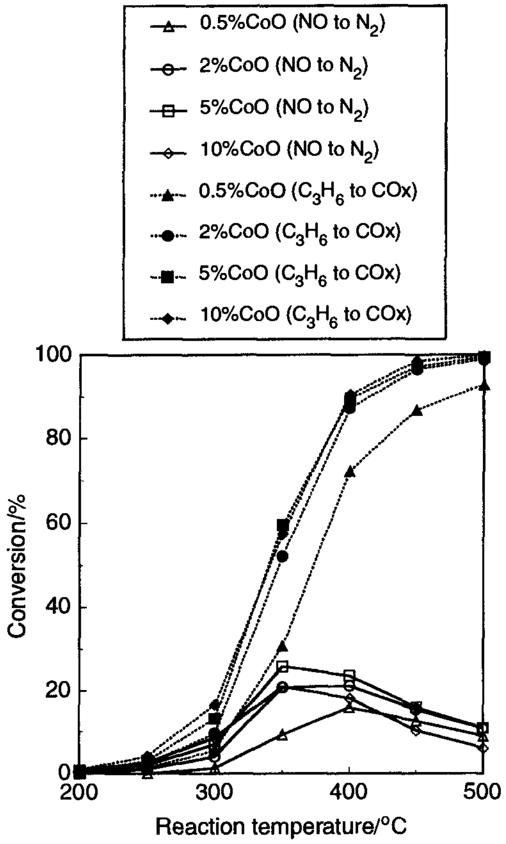

Fig. 3. Effect of cobalt loading on the activity of CoO(A)/SiO_2 calcined at 500°C in air. Reaction conditions: NO = 1000 ppm, C_3H_6 = 1000 ppm, O_2 = 10%, $W/F = 0.2\,g\,s\,cm^{-3}$.

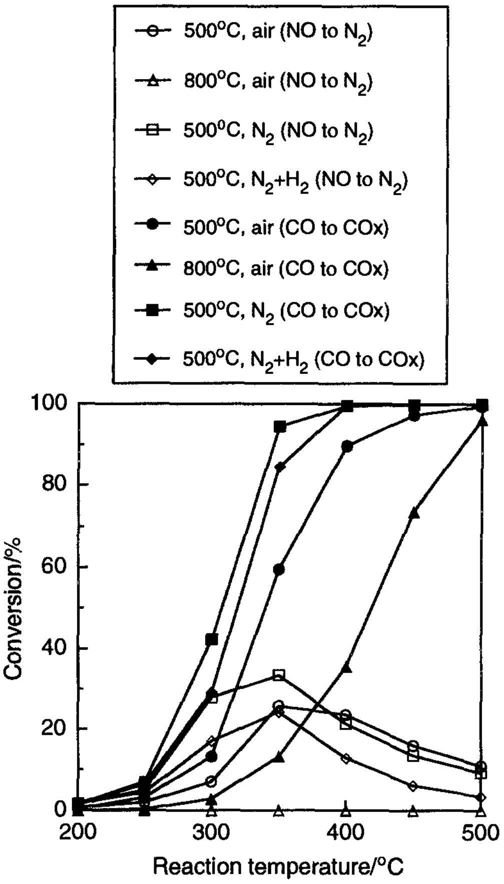

Fig. 4. Effect of calcination conditions on the activities of 5% CoO(A)/SiO_2. Reaction conditions: NO = 1000 ppm, C_3H_6 = 1000 ppm, O_2 = 10%, $W/F = 0.2\,g\,s\,cm^{-3}$.

It was found that calcination temperature and atmosphere have drastic effects on the performance of CoO(A)/SiO_2, as shown in fig. 4. Calcination at 800°C in air resulted in a complete loss of NO reduction activity with decreasing propene conversion to COx. With respect to calcination atmosphere, a highly active catalyst was obtained by calcination at 500°C in N_2. Propene conversion to COx on this catalyst was higher than on CoO(A)/SiO_2 calcined in air. Calcination in an H_2 plus N_2 atmosphere also increased the deNOx activity below 350°C but decreased the activity above this temperature.

3.3. Catalyst characterization

To obtain information on the catalytic active species, the catalyst samples were analyzed by various characterization techniques. Fig. 5 shows X-ray diffraction patterns of some of the CoO/SiO_2 samples. 5% CoO(N)/SiO_2(500, air) and CoO(Cl)/SiO_2(500, air) showed the pattern of Co_3O_4 crystal, indicating the presence of large Co_3O_4 particles, which are probably responsible for the low activity for NO reduction and high activity for propene oxidation. On the other hand, no diffraction peaks were observed for CoO(A)/SiO_2 except for CoO(A)/SiO_2 calcined at 800°C in air, which showed a clear pattern of crystal Co_2SiO_4. The low activity of this catalyst for both NO reduction and propene oxidation can be ascribed to a decrease of the number of the active sites by formation of large crystal Co_2SiO_4.

The X-ray photoemission spectra are presented in fig. 6. The presence of Co_3O_4 in CoO(N)/SiO_2(500, air)

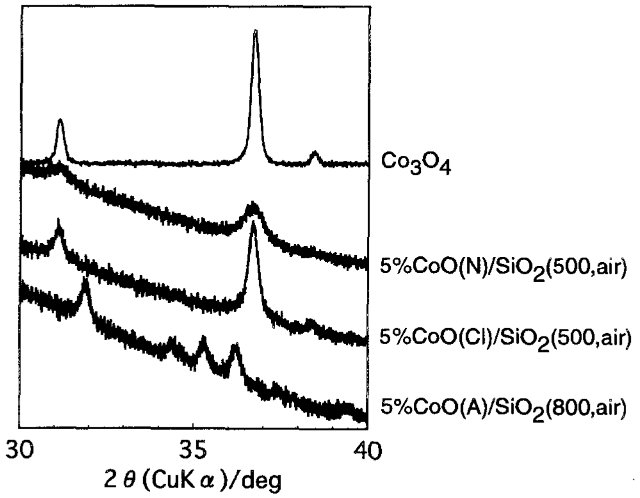

Fig. 5. X-ray diffraction patterns of CoO/SiO_2.

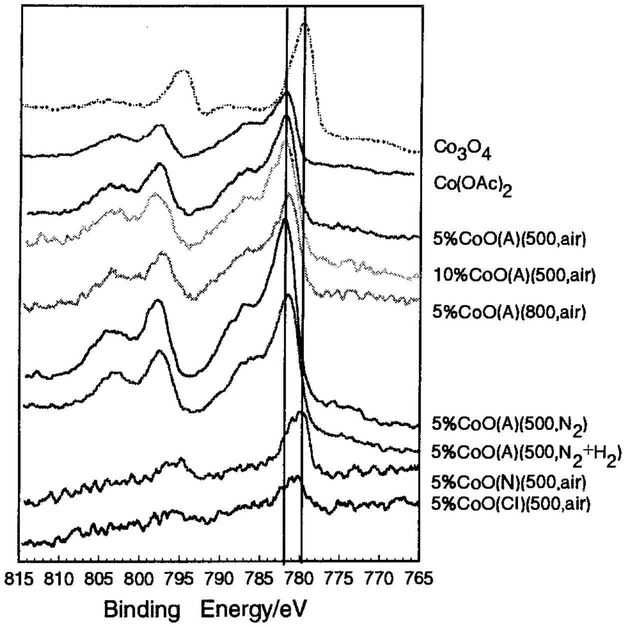

Fig. 6. X-ray photoemission spectra of CoO/SiO_2 catalysts in the region of Co 2p.

and $CoO(Cl)/SiO_2(500, air)$ was proved by the Co $2p_{3/2}$ binding energy. The low intensity of the peaks indicates that the dispersion of cobalt is low, which agrees well with the results of XRD measurements. The binding energy of all the $CoO(A)/SiO_2$ samples was very close to that of $Co(OAc)_2$. Also small satellite peaks located at about 6 eV higher than the main peak were observed. These results indicate that the cobalt species in these $CoO(A)/SiO_2$ samples is Co^{2+} ions.

NO chemisorption measurements were performed to get information on cobalt ion dispersion, since it was reported that NO is chemisorbed on surface cobalt ions. The results are presented in fig. 7. For $CoO(N)/SiO_2(500, air)$, $CoO(Cl)/SiO_2(500, air)$ and $CoO(A)/SiO_2(800, air)$, which showed clear X-ray diffraction patterns of Co_3O_4 or Co_2SiO_4, the amount of chemisorbed NO was quite small, suggesting very low cobalt dispersion. On the other hand, $CoO(A)/SiO_2$ samples calcined at 500°C adsorbed large amounts of NO. In particular $CoO(A)/SiO_2$ calcined in N_2 or N_2 plus H_2 atmospheres adsorbed quite large amounts of NO, indicating high cobalt ion dispersion.

Consequently, there seems to be a close relationship between the cobalt dispersion and the NO reduction activity. These results have led us to conclude that a highly dispersed surface Co^{2+} ion species is probably the main catalytic active species for the selective reduction. It is noted, however, that a linear relationship between the catalytic activity and the cobalt dispersion was not observed, as can be seen from the effect of cobalt loading. One of the reasons for this may be that there are other factors affecting the NO reduction activity, such as dispersion or ligand effect for the active Co^{2+} ions.

Okamoto et al. [9] also reported the presence of Co^{2+} species in cobalt/silica prepared from cobalt acetate. On the other hand, Co_3O_4 species is inactive for the selective reduction, although it catalyzes oxidation of propene. Similar results were observed by our group [10] for the selective NO reduction with propene over alumina-supported cobalt catalysts (CoO/Al_2O_3), for which the presence of large Co_3O_4 particles on the alumina promoted only hydrocarbon oxidation whereas CoO/Al_2O_3 with dispersed Co^{2+} ions in Al_2O_3 showed good activity for NO reduction. Although the activity of $CoAl_2O_4$ is not clear, it was confirmed in the present study that large Co_2SiO_4 crystals have very low catalytic activity mainly due to its low surface area.

Matsuzaki et al. [11] recenltly reported the activity of Co/SiO_2 catalysts for CO hydrogenation. According to their results, the activity strongly depended on the cobalt presursor. The cobalt in Co/SiO_2 prepared from cobalt acetate was considered to be in the form of a stable entity through its combination with the oxygen of silica. This agrees well with the present results. At the moment, it is not clear why cobalt acetate gives highly

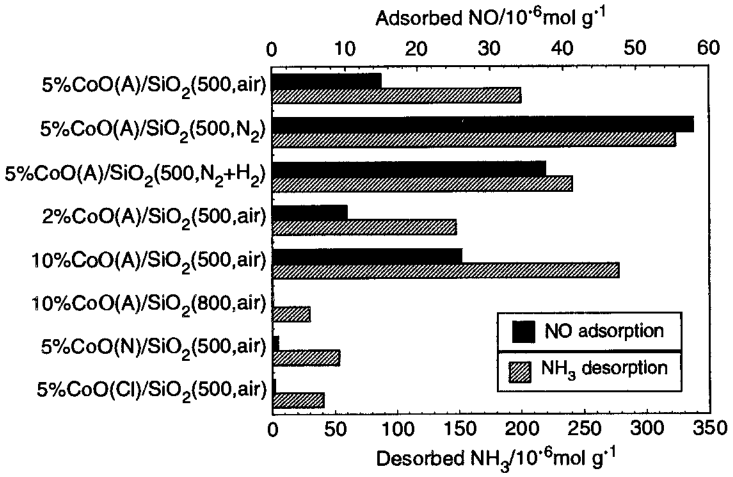

Fig. 7. Results of NO chemisorption and NH_3-TPD measurements.

dispersed cobalt ion species on silica. But this is probably because the acetate moiety has higher affinity to silica than that of nitrate or chloride by its strong coordinating power.

Ammonia TPD measurements were also done to measure the solid acid properties of the catalyst surface. No noticeable differences in the position of the TPD peaks were observed for most of the CoO/SiO_2 samples. The amount of desorbed ammonia given in fig. 7, which corresponds to the acid amount, was almost proportional to the amount of chemisorbed NO. This suggests that the dispersed Co^{2+} ions have some solid acid property, which may be responsible for the catalytic activity.

There have been many arguments regarding the catalytic active sites for selective NO reduction with hydrocarbons [12]. But the sites are more complex than in many catalytic reactions. For example, catalytic sites for NO oxidation, acid sites for activation of the hydrocarbon, and metal ions for activation of oxygen are considered to be important. In the present case, dispersed Co^{2+} ions appear to act as a single catalytic species for NO reduction like an alumina catalyst. Possibly the ions may have all the qualities of the above-mentioned active sites.

3.4. Reaction pathway

The reaction pathway of NO reduction over 2% $CoO(A)/SiO_2$ (500, air) was investigated. The results of various reactions on this catalyst are summarized in fig. 8. It was discovered that N_2 formation through NO_2 reduction was smaller than that through NO reduction in the whole temperature range. Moreover, propene conversion to COx was higher for NO_2 reduction. Therefore, the oxidation of NO to NO_2 is not the rate-determining step in the present overall selective reduction of NO. This is in contrast to alumina-catalyzed NO reduction.

It can be seen from fig. 8 that the propene conversions for the $NO–C_3H_6–O_2$ reaction are almost the same as those for the $C_3H_6–O_2$ reaction. This indicates that the selective reduction of NO takes place at the temperatures where the oxidation of propene with oxygen proceeds. Therefore we think that the reduction of NO to N_2 proceeds mainly through the following pathway. The first step is the oxidation of propene by oxygen to some kind of oxygenated intermediate, which is rate-determining. Then, N_2 is formed via several steps from the intermediate and NOx:

$$C_3H_6 \xrightarrow{+O_2} [C_xH_yO_z] \xrightarrow{+NOx} N_2 + COx + H_2O$$

4. Summary

Although transition metal oxides catalyze only hydrocarbon oxidation, some silica-supported transition metals prepared from metal acetates showed good activity for the selective reduction of NO. Among the 4th period transition metal/SiO_2 catalysts, CoO/SiO_2 showed the highest activity. The preparation conditions exerted drastic effects on the activity of CoO/SiO_2. For example, calcination at high temperatures resulted in a complete loss of NO reduction activity, whereas calcination in a nitrogen atmosphere gave a highly active catalyst. Catalyst characterization using XRD, XPS, and NO chemisorption measurements suggested that highly dispersed Co^{2+} ions having solid acid properties, are the catalytic active species. It was suggested that the rate-determining reaction step of the overall selective reduction of NO is the oxidation of propene by oxygen to partially-oxidized hydrocarbons.

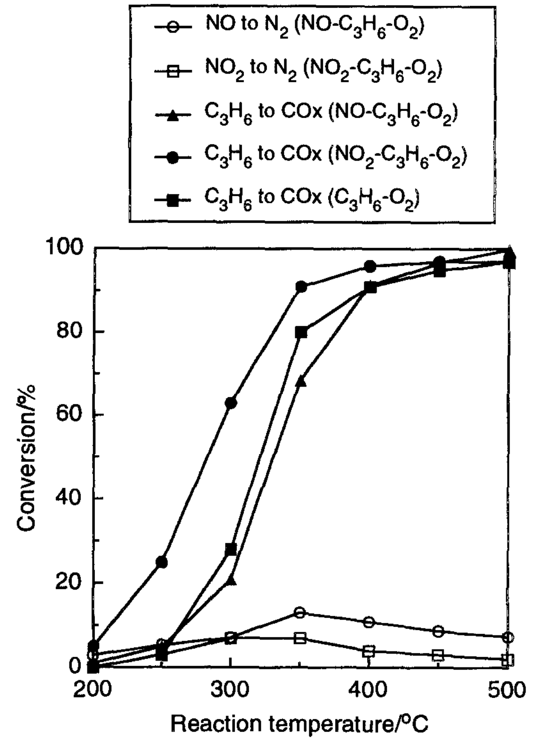

Fig. 8. Activities of 2% $CoO(A)/SiO_2(500)$ for various reactions. Reactions conditions: NO = 1000 ppm, C_3H_6 = 330 ppm, O_2 = 10%, $W/F = 0.2\,g\,s\,cm^{-3}$.

Acknowledgement

We would like to express our sincere thanks to Mr. Mitsunori Tabata of Cosmo Research Institute for his assistance in NO chemisorption measurements.

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