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Selective Reduction of NO with CO Over Titania Supported Transition Metal Oxide Catalysts

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Abstract A series of transition metal oxides promoted titania catalysts (MO_x/TiO_2; M = Cr, Mn, Fe, Ni, Cu) were prepared by wet impregnation method using dilute solutions of metal nitrate precursors. The catalytic activity of these materials was evaluated for the selective catalytic reduction (SCR) of NO with CO as reductant in the presence of excess oxygen (2 vol.%). Among various promoted oxides, the MnO_x/TiO_2 system showed very promising catalytic activity for NO + CO reaction, giving higher than 90% NO conversion over a wide temperature window and at high space velocity (GHSV) of 50,000 h^{-1}. It is remarkable to note that the catalytic activity increased with oxygen, up to 4 vol.%, under these conditions leading primarily to nitrogen. Our TPR studies revealed the presence of mixed oxidation states of manganese on the catalyst surface. Characterization results indicated that the surface manganese oxide phase and the redox properties of the catalyst play an important role in final catalytic activity.

Keywords Manganese oxides (MnO_x) · Titania (TiO_2) · Carbon monoxide (CO) · Nitric oxide (NO) · Selective catalytic reduction (SCR)

1 Introduction

Nitrogen oxides (NO_x) are major environmental pollutants and show detrimental effects on human health. NO is the major component of NO_x and it is generated in combustion processes (stationary and mobile) [1, 2]. Catalytic reduction of NO_x (SCR) is the most popular among other NO_x abatement technologies like storage and thermal decomposition. The most common reductants for SCR are ammonia, urea, CO, H_2 and hydrocarbons like methane, ethane and propylene [2]. Using carbon monoxide as reductant offers some distinct advantages since it can be produced onsite for the cases of coal or natural gas utilization (stationary sources), or it is part of the exhaust stream due to incomplete combustion of the liquid fuel (mobile sources). In this manner, one can eliminate the costly steps of purchasing, transporting and storing the reductant. The vast majority of the catalysts reported for the NO + CO reaction are supported platinum group metals (Pt, Pd, Rh, Ir) [3–5], perovskite type oxides [6, 7], and supported copper oxide [8]. Most of the reported catalysts require a high working temperature (773–873 K) to get reasonably high NO conversions. Furthermore, the activity of those catalysts significantly decreases in the presence of oxygen, which is a component of any flue gas stream. In recent years, MnO_x-based catalysts attracted much attention due to their high activity for various reactions such as, oxidative coupling of methane [9], CO and CH_4 oxidation [9, 10], oxidative dehydrogenation [11, 12], total oxidation of VOCs [13, 14].

In our previous studies we found that MnO_2/TiO_2 is extremely active catalyst for the SCR of NO with NH_3 at low temperatures [15, 16]. In the present study we have screened a number of transition metal oxides namely CrO_x, MnO_x, Fe_2O_3, NiO and CuO supported on high surface area anatase titania for the NO + CO reaction. Our main emphasis in the present study is to replace expensive platinum group metals with inexpensive transition metal oxides and carryout the reaction selectively in a wide temperature range under real flue gas conditions using excess oxygen. For this purpose, a series of transition metal

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oxide catalysts, (Cr, Mn, Fe, Ni and Cu) loaded on titania catalysts were prepared by wet impregnation method. The prepared catalysts were thoroughly characterized by various physicochemical techniques. Among various catalysts, the MnO_x/TiO_2 system showed very promising catalytic activity for NO + CO reaction by exhibiting conversions higher than 90% over a wide temperature window and at high space velocity (GHSV) of 50,000 h^{-1} and in the presence of relatively high concentrations of oxygen and the reaction was highly selective in the presence of oxygen. Moreover, we found that by increasing the oxygen up to 4 vol.%, the catalytic activity increases monotonically. TPR studies revealed the presence of mixed oxidation states of manganese on the catalyst surface and the surface manganese oxide undergoes step wise reduction.

2 Experimental Section

2.1 X-ray Diffraction

X-ray powder diffraction patterns have been recorded on a Siemens D500 diffractometer using a Cu K_α radiation source (wavelength 1.5406 Å). An aluminium holder was used to support the catalyst samples. The scanning range was $5°-70°$ (2θ) with a step size of 0.05° and a step time of one second. The XRD phases present in the samples were identified with the help of JCPDS data files.

2.2 BET Surface Area

The specific surface areas of the samples were determined on a Micromeritics 2360 instrument by nitrogen physisorption at liquid nitrogen temperature (77 K) and by taking 0.162 nm^2 as the molecular area of the nitrogen molecule. All samples were degassed at 200 °C under vacuum before analysis.

2.3 Temperature Programmed Reduction (H_2-TPR)

The temperature-programmed reduction (H_2-TPR) experiments were carried out from 70 to 900 °C on a Micromeritics AutoChem 2910 instrument using 50 mg of calcined catalyst. Prior to the analysis the catalysts were pretreated at 250 °C for 2 h in ultra high pure helium (30 ml min^{-1}) stream. The TPR runs were carried out with a linear heating rate (10 °C/min) in a flow of 4% H_2 in argon with a flow rate of 25 ml min^{-1}. The hydrogen consumption was measured quantitatively by a thermal conductivity detector.

2.4 Ammonia TPD

The ammonia TPD experiments were performed on a Micromeritics AutoChem 2910 instrument using 50 mg of catalyst. Prior to the experiments the catalysts were pretreated at 250 °C for 1 h in an ultra high pure He (30 ml min^{-1}) stream. The furnace temperature was lowered to 100 °C, and the samples were then saturated with anhydrous NH_3 (4% in He) at a flow rate of 30 ml min^{-1} for 1 h. Physisorbed NH_3 was removed by flushing the catalyst with helium at 100 °C for 2–3 h before starting the TPD experiments. The heating rate for the TPD measurements was 5 °C min^{-1} and the temperature ranged from 100 to 700 °C.

2.5 Catalyst Synthesis

A series of anatase titania supported transition metal oxide (M = Cr, Mn, Fe, Ni, Cu) catalysts were prepared by wet impregnation method. The titania used in this study was Hombikat UV 100 from Sachtleben Chemie. The transition metal oxides were deposited on titania using highly dilute solutions of their nitrate precursors. In a typical synthesis 50 ml deionized water was added to a 100 ml beaker containing a measured quantity of support. The mixture was heated to 70 °C under constant stirring. Then, a predetermined quantity of nitrate precursor was added to the solution and mixture was evaporated to dryness. The paste obtained was further dried overnight at 110 °C, ground and calcined at 500 °C for 4 h in a flow of air.

2.6 Reaction Procedure

The SCR of NO with CO was carried out at atmospheric pressure in a fixed bed quartz reactor (i.d. 6 mm). A measured amount of catalyst (0.1 g, 80–120 mesh) was placed in the reactor in between two glass wool plugs. Oxygen (Wright Bros., 4% in He), carbon monoxide (Matheson, 1% in He) and nitric oxide (Air Products, 2.0% in He) were used as received. The inlet concentrations of NO and CO were 400 ppm. Two volume percentage of oxygen was fed into the reaction stream. All the experiments were conducted at the gas hourly space velocity of 50,000 h^{-1}. The reaction temperature was measured by a type K thermocouple inserted directly into the catalyst bed. Prior to the catalytic experiments, the catalyst was activated in-situ by passing oxygen for 2 h at reaction temperature. The reactants and products were analyzed online using a Quadrapole mass spectrometer (MKS PPT-RGA), chemiluminescence detector (Eco Physics CLD 70S) and a gas chromatograph equipped with TCD and Porapack Q and Carboxen columns.

3 Results and Discussion

The powder X-ray diffraction patterns of various titania supported transition metal oxide samples calcined at 500 °C are shown in Fig. 1. All the samples showed broad diffraction lines due to the anatase phase of titania (JCPDS file no. 21–1272). No independent lines from crystalline promoters are observed in the XRD patterns, except for Cu/TiO_2. This indicates that the promoted oxides are well dispersed on the titania support, and they are in amorphous or poorly crystalline state. However, low intensity copper oxide lines are observed in the XRD pattern of Cu/TiO_2, indicating the presence of crystalline copper oxide in the sample. XRD studies revealed that the promoter oxide does not promote any titania phase transformation (anatase to rutile). Specific surface areas and the total acidity values of the prepared catalysts are presented in Table 1. The pure titania support exhibited a high specific surface area of 309 m^2/g. However, the specific surface areas of the transition metal oxide promoted samples calcined at 773 K showed much lower BET surface area than the pure TiO_2 support. This is in agreement with previous literature reports where impregnated metal oxide species were found to decrease the surface area of the TiO_2 [10]. This severe loss in the surface area could be attributed to the blocking of micropores of titania support by deposited metal oxides.

The redox behavior of prepared catalysts was studied by temperature programmed reduction (H_2-TPR) technique and the corresponding TPR profiles are presented in Fig. 2.

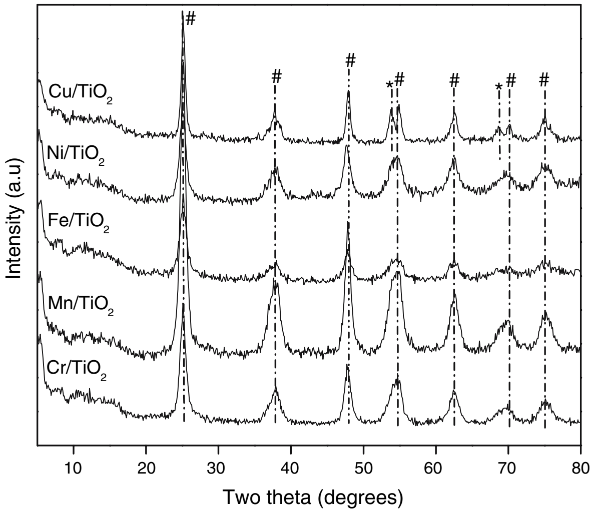

Fig. 1 Powder X-ray diffraction patterns of various titania supported transition metal oxide catalysts. (#) is due to anatase titania; (*) is due to CuO

Table 1 Surface area and total acidity values of prepared catalysts

S. no	Sample	BET surface area (m^2/g)	Total acidity (mmol g^{-1})
1	TiO_2	309	–
2	Cr_2O_3/TiO_2	190	1.33
3	MnO_2/TiO_2	187	0.93
4	Fe_2O_3/TiO_2	199	0.75
5	NiO/TiO_2	169	0.75
6	CuO/TiO_2	55	0.5

Figure 2 shows that the reduction temperatures of all titania supported oxides are decreased when compared to the pure individual promoter oxides. The reduction profile of pure CuO is characterized by a single reduction peak at 380 °C [17]. In the present study, Cu/TiO_2 system showed two reduction peaks and the reduction maximum is shifted to low temperatures indicating a strong interaction between the titania support and the promoted copper oxide. Low temperature peak is due to well dispersed CuO on TiO_2

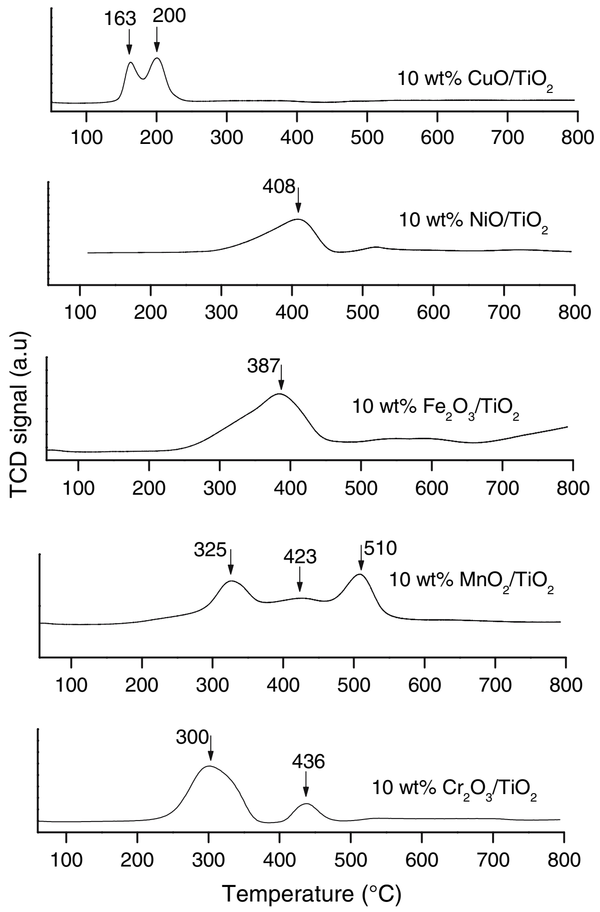

Fig. 2 H_2-TPR patterns of titania supported transition metal oxide catalysts

support and high temperature peak is due to the reduction of bulk crystalline CuO. From the TPR results it is confirmed that two kinds of CuO is present on the catalyst surface, one is the bulk CuO which shows no interaction with the support, and the other is CuO interacted with the support. These results are in good agreement with earlier literature reports [18]. In the case of Ni/TiO_2 sample two reduction peaks are observed at 408 and 520 °C. In Ni/Ti samples NiO is directly reduced to metallic nickel in a single step. The low temperature peak could be attributed to the reduction of NiO to Ni. Whereas the reduction peak at 520 °C is due to the partial reduction of titania support (Ti^{4+} to Ti^{3+}) which is in interaction with promoted NiO species. The presence of Ni^{3+} was not observed in the present study which can be confirmed by the absence of a reduction peak at 200 °C [19]. Fe/TiO_2 sample showed three reduction peaks due to the consecutive reduction of $Fe_2O_3 \rightarrow Fe_3O_4 \rightarrow FeO \rightarrow Fe$. Three distinct reduction peaks are observed for the most active Mn/TiO_2 sample. The low temperature reduction peak at 325 °C is due to the reduction of MnO_2 to Mn_2O_3. This peak also contributes to the reduction of Ti^{4+} to Ti^{3+}, because at low loadings manganese enters into the titania lattice [20]. Two additional peaks at temperatures 423 and 510 °C are due to the reduction of Mn_2O_3 to Mn_3O_4 and Mn_3O_4 to MnO. Further reduction of MnO is not possible due to thermodynamic reasons under the applied experimental conditions [21]. The TPR results revealed that the Mn/TiO_2 sample manganese oxide undergoes the consecutive reduction of $MnO_2 \rightarrow Mn_2O_3 \rightarrow Mn_3O_4 \rightarrow MnO$. Cr/TiO_2 catalyst also showed two reduction peaks in the temperature range of 280–480 °C. Pure CrO_3 shows a single reduction peak at 390 °C ($Cr^{6+} \rightarrow Cr^{3+}$) [22]. The presence of titania decreased the reduction temperature of chromia. The low temperature peak at 300 °C is attributed to the reduction of Cr^{6+} to Cr^{3+} and the peak at 436 °C is due to the reduction of Ti^{4+} to Ti^{3+} because of the interaction of chromia with titania support. Reduction of CrO_3 strongly depends on the support nature. It is known that Cr/Al_2O_3 shows only one reduction peak where as Cr/TiO_2 shows two reduction peaks [23]. Fountzoulz et al. [24] reported that, mono chromate species formed on anatase titania support are responsible for high SCR activity of NO with NH_3 as reductant at high temperatures. It is known that anatase titania cannot be reduced even at higher temperatures. However, in the present study reduction of titania support was observed for Cr/TiO_2, Mn/TiO_2 and Ni/TiO_2 samples. This is due to the interaction between support and dispersed promoter oxide by the formation of M–O-support functionalities [25].

The acid strength distribution of the prepared catalysts was determined using ammonia TPD technique. The TPD patterns of these catalysts are shown in Fig. 3 and the corresponding total acidity values are presented in Table 1. Broad acid site distribution is observed for Cr/TiO_2, Fe/TiO_2 and Ni/TiO_2 samples. The Cu/TiO_2 sample showed a temperature maximum at 600 °C indicating the presence of strong acid sites. Expect Mn/TiO_2, all other samples showed two temperature maxima indicating the presence of two types of acid sites with different acid strengths. It is known in the literature that anatase titania possesses purely Lewis acid sites [26]. Our previous ammonia adsorbed FT-IR studies on various transition metal oxides promoted titania catalysts revealed that the Cr/TiO_2 sample posseses large amount of Brönsted acid sites and the highest surface acidity [16]. The present study confirmed the above observations where highest amount of ammonia was desorbed from Cr/TiO_2 sample (Table 1). Ammonia FT-IR studies also indicated that Mn/TiO_2 and Cu/TiO_2 catalysts posses significant amount of Lewis acid sites. Kapteijn et al. [27] also observed the same phenomenon with manganese oxide promoted alumina catalysts where the addition of manganese does not induce any Brönsted acidity in the system. Accordingly, these two catalysts showed good catalytic activity for CO + NO reaction.

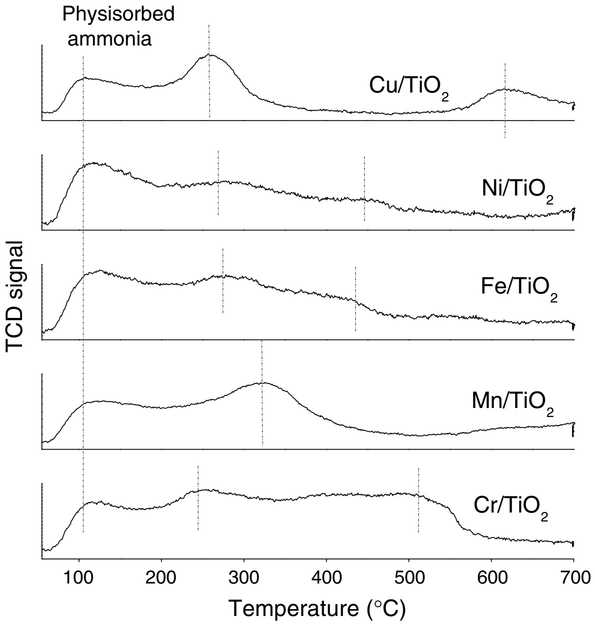

Fig. 3 Ammonia-TPD profiles of prepared samples

Catalytic activity results for the SCR of NO with CO at 200 °C over various transition metal oxides supported on TiO_2 are presented in Fig. 4. Under identical operating conditions 10 wt.% manganese supported on TiO_2 showed excellent performance giving more than 90% NO conversion even in the presence of oxygen and at very high space velocity (GHSV = 50,000 h^{-1}). In our

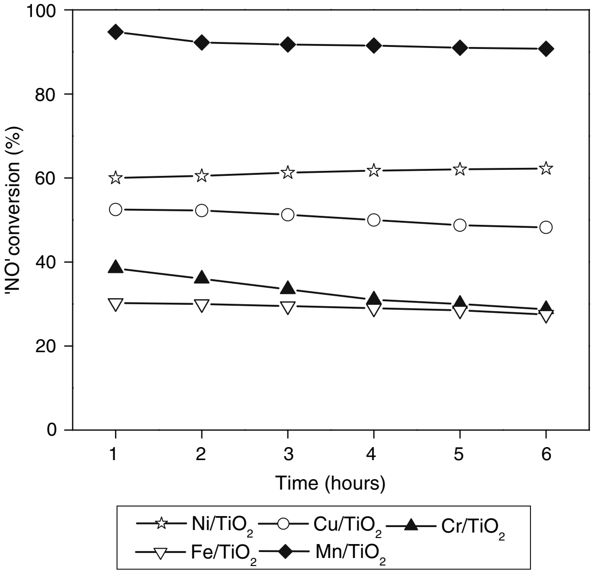

Fig. 4 Catalytic activity of various titania supported catalysts at 200 °C. NO = CO = 400 ppm, 2 vol.% oxygen in feed, GHSV = 50,000 h^{-1}

previous studies we have reported 100% NO conversion and complete N_2 selectivity at low temperature (175 °C) over MnO_2/TiO_2 catalyst using ammonia as reductant [16, 20]. Moreover, the activity of this catalyst remains stable even in the presence of 2 vol.% oxygen and 11 vol.% water vapor in the feed [20]. The high activity of MnO_x can be attributed to its ability to form variable oxidation states of manganese (MnO_2, Mn_2O_3, Mn_3O_4 and MnO) and its oxygen storage capacity [28]. MO_x compounds contain very labile lattice oxygen in their berthollide structure. The catalytic activity of supported manganese oxides strongly depends on manganese oxide phase, precursor, loading, calcination temperature and the nature of the support [27–31]. Manganese nitrate and manganese acetate are the commonly used manganese precursors. It is known that manganese nitrate precursor and low calcination temperature favor MnO_2 formation, while manganese acetate precursor and high calcination temperatures favor Mn_2O_3 and Mn_3O_4 phases [28–31]. In our previous studies we observed that support also plays a crucial role in determining the manganese oxide phase. In various titania supported MO_x catalysts, we observed that anatase titania favors the MnO_2 phase, where as rutile titania favors the formation of Mn_2O_3 [32]. The reducibility of manganese oxides changes also with the support nature. According to Arena et al. [33] reducibility of manganese oxide on various commonly used supports change in the following manner: $MnO_x/ZrO_2 > MnO_x/Al_2O_3 > MnO_x/TiO_2 > MnO_x/SiO_2$. It is also known that MnO_2 exhibits higher NO reduction activity than Mn_2O_3 when ammonia is used as reductant [34]. However, in the present study we have not observed any crystalline MO_x on titania support. Low manganese oxide loading could be the reason for this behavior. These results are in line with our previous studies, where we have reported the formation of crystalline manganese oxide only for loadings above 11.5 wt.% [20]. There are some reports in the literature that the addition of ceria to support or noble metal efficiently promotes the CO + NO reaction [35–37]. Ceria is well known for its oxygen storage capacities and constitutes a main component in three way catalysts (TWC) [38, 39]. In the present study we have also carried out the CO + NO reaction with 10 wt.% CeO_2 promoted MnO_x/TiO_2 catalysts. In contrast to literature reports, the activity has been decreased for ceria promoted samples. These results are shown in Fig. 5. The decrease in the activity could be attributed to the oxidation of CO, since CeO_2–TiO_2 based materials are well known CO-oxidation catalysts [40].

It is remarkable to note that the SCR activity of 10 wt.% MnO_x/TiO_2 catalyst is increased and quite stable in the presence of oxygen, which consists a major component in real flue gas. In general, oxygen shows strong inhibitory effect on NO reduction activity and NO + CO reaction is non-selective in the presence of oxygen due to the competition between NO and oxygen for CO. However, in the present study NO + CO reaction is highly selective over MnO_x/TiO_2 catalyst even in the presence of excess oxygen. The comparison of activities among various promoted transition metal oxides indicates that titania supported manganese oxide show highly promising NO reduction activity in the presence of oxygen at 200 °C.

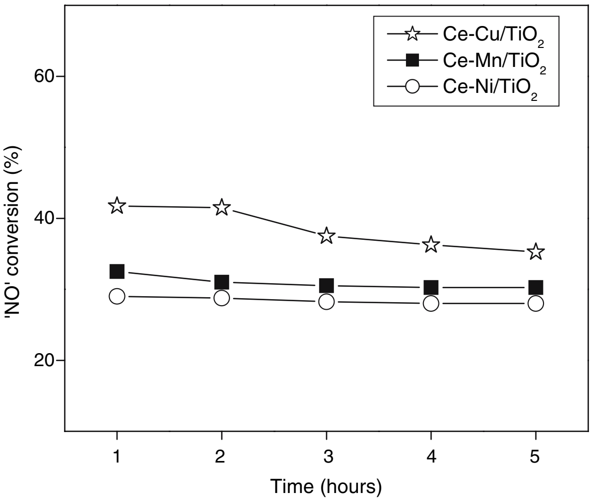

Fig. 5 Catalytic activity of 10 wt.% CeO_2 promoted MO_x/TiO2 samples. NO = CO = 400 ppm, 2 vol.% oxygen in feed, GHSV = 50,000 h^{-1}

4 Conclusions

Comparison of activities among selected promoted transition metal oxides (Cu, Ni, Fe, Mn, Cr) indicates that titania supported manganese oxide show promising NO reduction activity in the presence of oxygen at the temperature of 200 °C. It is remarkable to note that the SCR activity of 10 wt.% MnO_x/TiO_2 catalyst is increased and quite stable in the presence of oxygen. In the present study, NO + CO reaction leading to the formation of N_2 and CO_2 is highly selective over MnO_x/TiO_2 catalyst even in the presence of oxygen. Our characterization results revealed that the high surface area, the redox nature of the catalyst and manganese oxide phase play an important role in achieving high activity for CO + NO reaction. This procedure can be applied to stationary and/or mobile sources of NO_x.

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