Remediation of various naturally oxygenated volatile organic compounds (O-VOCS) by Mn- and Cr-supported γ-Al$_2$O$_3$ nanocatalysts

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The catalytic combustions of different naturally oxygenated volatile organic compounds (ethyl acetate, isopropanol, methyl ethyl ketone (MEK), and benzyl alcohol) alone and in binary mixtures were investigated over pure γ-Al$_2$O$_3$, Mn/γ-Al$_2$O$_3$, and Cr/γ-Al$_2$O$_3$. The catalysts were prepared by the wet impregnation method and were characterized using XRD, ICP-AES, SEM, and BET. Mn/γ-Al$_2$O$_3$ showed higher activity than others in combustion of the O-VOCs, whereas complete conversion of isopropanol (the most reactive O-VOC) occurred at 350 $^\circ$C and 400 $^\circ$C on Mn/γ-Al$_2$O$_3$ and Cr/γ-Al$_2$O$_3$, respectively. The following order was found for reactivity of organic compounds in single form: isopropanol > benzyl alcohol > ethyl acetate > MEK. There was no relation between activity of the catalyst and BET surface area. An inhibition/promotion effect was found in the oxidation of O-VOC binary mixtures because of the competitive adsorption on the catalyst, leading to an oxidation behavior for O-VOC binary mixtures different than that of single components. The presence of water vapor as a co-feed had an inhibition effect on isopropanol oxidation and was temperature-dependent such that it decreased above 350 $^\circ$C.

Key Words: Oxygenated organic compounds, catalytic oxidation, Mn/γ-Al$_2$O$_3$, Cr/γ-Al$_2$O$_3$, nanocatalyst

Introduction

Volatile organic compounds (VOCs) are an important class of air pollutants, emitted from many industrial processes and transportation activities; they are considered a major source of direct (toxicity, order) or indirect

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(smog) pollution of air.[1,2] There are many different techniques for VOC removal. Thermal combustion is the most extended method for abatement of VOCs, but it is not a feasible process as it operates at a high temperature, usually above 1273 K. It requires additional fuel and the use of temperature-resistant materials, and it generates noxious byproducts (NO_x). Catalytic combustion appears to be the most promising solution for elimination of VOCs when they are at low concentrations. Catalytic combustion offers environmental advantages, since it operates at much lower temperatures, avoiding formation of nitrogen oxides.[3,4]

Base metal oxides, like Cu, Mn, and Cr, and supported noble metals catalysts (Pt, Pa) have been used so far in catalytic combustion of VOCs. The high cost of noble metals has increased the interest in substitution, since transitive metal oxides may fulfill the requirements. These transition metals can be considered environmental friendly. The interaction of manganese with the support as well as with other compounds present in the catalyst significantly influences the bulk and surface structure.[5]

Increased dispersion of MnO_x on the support surface leads to significant increases in catalytic activity. This is attributed to a larger catalyst surface area being exposed to the reaction feed. MnO_x showed an interesting behavior in the catalytic combustion of hydrocarbons and oxygenated volatile organic compounds (O-VOCs).[6] Chromium is the most active metal among the transition metals.[7] The choice of the support is also an important factor influencing the conversion of organic compounds.

An important property pointed out by several authors is the hydrophobic nature of the support.[8] The advantage of using a hydrophobic support is that moisture, both that from the atmosphere and that formed as a reaction product, will not adsorb onto the catalyst, particularly at low reaction temperatures. γ-Al_2O_3 is commonly used as an adsorbent and a catalyst or catalyst support in many chemical processes, including the cracking, hydrocracking, and hydrodesulfurization of petroleum feed stocks. It is perhaps the most important for catalytic applications.[9,10] The utility of γ-Al_2O_3 can be traced to a favorable combination of textural properties (i.e. surface area, pore volume, and pore size) and acid-base characteristics. The conventional forms of γ-Al_2O_3 typically exhibit a BET surface area of less than 250 m^2/g.[9]

$\gamma-Al_2O_3$ and transition-metal-supported γ-Al_2O_3 catalysts have been used to study catalytic oxidation of volatile organic compounds.[11,12] The catalytic oxidation of toluene over γ-Al_2O_3-supported transition metal oxide catalysts has been investigated employing a fixed-bed flow reactor.[13] S.C. Kim studied the catalytic oxidation of benzene, toluene, and xylene (BTX) over (Cu, Mn, Fe, V, Mo, Co, Ni, Zn)/γ-Al_2O_3,[14] and the oxidation of ethanol on pure alumina and K-Mn/γ-Al_2O_3 oxides was studied by Peluso et al.[6]

Most studies of the catalytic oxidation of VOCs over γ-alumina have been restricted to nonoxygenated compounds. However, some of the main industrial solvents are oxygenated volatile organic compounds. Oxygenated VOCs can be defined as volatile organic compounds that contain functional groups associated with oxygen atoms. For O-VOCs, oxidation reaction mechanisms and their interactions with catalyst surfaces are different than those of common VOCs. Few studies have been done on the catalytic combustion of O-VOCs on γ-Al_2O_3 and metal oxides supported on γ-Al_2O_3.[15,16]

In this work, for the first time, catalytic oxidations of 4 different types of O-VOCs, namely ethyl acetate, isopropanol, methyl ethyl ketone (MEK), and benzyl alcohol, over γ-Al_2O_3-based catalysts were studied. These O-VOCs are common solvents in the chemical and petrochemical industries.[17,18] Among the transition metals, manganese and chromium were selected because of their higher catalytic activity and their various oxidation states, and Mn/γ-Al_2O_3 and Cr/γ-Al_2O_3 catalysts were prepared.

This paper was aimed at studying the oxidation of O-VOCs over pure γ-Al_2O_3, Mn/γ-Al_2O_3, and Cr/γ-Al_2O_3 in single forms and binary mixtures. The influences of a few effective parameters of catalytic activity were also studied. These catalysts were first characterized by ICP-AES, BET, XRD, and SEM, and then the catalytic studies were investigated.

Material and methods

Preparation and characterization of catalysts

Commercial γ-Al_2O_3 powder (BET: approximately 190 cm^2/g) was supplied by Merck and was used as a pure γ-Al_2O_3 catalyst without further purification or treatment. Mn/γ-Al_2O_3 catalyst was prepared with the conventional wet impregnation method through immersing γ-Al_2O_3 in 0.5 M $Mn(NO_3)_2$ solution for 24 h followed by filtration, drying, and calcinations at 450 °C for 4 h. A similar procedure was followed for the preparation of the Cr/γ-Al_2O_3 catalyst.

The catalysts were characterized by XRD, BET, ICP-AES, and SEM techniques. X-ray diffraction (XRD) studies were carried out on a Siemens D500 diffractometer working with a K_α line of copper ($\lambda = 0.154$ nm) at a scan rate of 4°/min. Measurements of the samples were carried out in the 2θ range of 5°-70°. The mean crystallite sizes were estimated using the Scherrer formula, $D = K\lambda/\beta \cos\theta$, where K = 0.89, $\lambda = 0.15418$ nm, β is the half peak width of the X-ray reflection, and θ is the diffraction angle.[18]

The content of Cr and Mn species loaded in Cr/Al_2O_3 and Mn/Al_2O_3 were determined by inductively coupled plasma atomic emission spectroscopy (ICP-AES) using an Integra XL (GBC, Australia) instrument.

Brunauer, Emmet, and Teller (BET) surface areas of the samples were determined by N_2 adsorption-desorption at -196 °C using a Micromeritics (Gemini 2375) surface area analyzer, assuming a value of 0.164 nm^2 for the crosssectional area of the nitrogen molecule.

Furthermore, the shape and size of the particles were determined via scanning electron microscopy (SEM) with an EQ-C1-1 instrument, precoating the samples with gold.

Analytical methodologies used

The catalytic activities of the catalysts were tested by combustion of O-VOCs in a continuous fixed bed reactor working under atmospheric pressure.

The reactor consisted of 0.8 cm i.d. U-shaped quartz, placed in an electric furnace with a proportional-integral-derivative controller (PID). The catalyst (0.2 g) was placed over a plug of quartz wool, and a thermocouple was placed inside the catalyst bed. Before starting each run, the catalysts were pretreated with 10 mL/min of pure nitrogen at 473 K in order to eliminate the possible compounds adsorbed on the catalyst surface.

The concentration of VOCs in the gaseous feed was 0.2% mol/mol. Measurements were taken from 200 °C to 500 °C. Different temperatures were randomly tested in order to avoid the variation of catalyst properties or hysteretic effects. The flow of gases was controlled by a needle valve (Parker Company, USA). A bubbling saturator was used to evaporate VOCs. Nitrogen was used as a carrier gas, and flow rates were measured using a calibrated soap bubble flow meter. All experimental runs were carried out under steady state conditions.

Catalytic activity measurements were carried out with a Shimadzu 2010 gas chromatograph apparatus with a flame ionization detector (FID). In order to meet the requirement of adsorption at infinite dilution, corresponding to zero coverage and GC linearity[19], amounts injected were about 1 μL. For each measurement, at least 3 repeated injections were taken to obtain reproducible results. Air was used as a marker for the retention time correction, which was used to ensure the absence of dead volume when a new column was placed in the chromatograph. The by-products produced during O-VOC oxidation were characterized in trapped samples by gas chromatography-mass spectrometry (GC-MS) (Agilent 6890N).

Result and discussion

Characterization of catalysts

ICP-AES results showed a manganese content of 4% (wt.) in Mn/γ-Al_2O_3. BET surface areas of Mn/γ-Al_2O_3 (145.5 m^2/g) decreased in comparison to the surface area of pure γ-Al_2O_3 (190 m^2/g). In the case of Cr/γ-Al_2O_3, the chromium loading was also determined to be approximately 4% (wt.), whereas the BET surface area of the catalyst decreased to 142 m^2/g. The accuracy, precision, and detection methods of these Cr and Mn measurements are presented in Table 1.

Table 1. Results of ICP-AES.

Measured element	Amount (w/w %)	Precision (% RSD)	Accuracy (relative %)	Detection limit (parts per billion)
Cr	4.03	1.61	2.02	20
Mn	4.05	1.59	1.56	2

The SEM images of pure γ-Al_2O_3, Cr/γ-Al_2O_3, and Mn/γ-Al_2O_3 are shown in Figure 1. From images of commercial γ-Al_2O_3 (Figures 1a and 1b, at 2 different resolutions), we can conclude that the powder contained the sintered particles, and this result can be accepted if Figures 1a and 1b are compared. However, the particle size (<100 nm) and dispersion of the catalysts, as shown in Figures 1c and 1d, would be favorable for catalytic activity in the combustion of VOCs. In addition, from the images, we can conclude that the particles of the manganese oxide of Mn/γ-Al_2O_3 were better dispersed than the particles of Cr/γ-Al_2O_3.

The XRD patterns of the catalysts are shown in Figure 2. There was not much difference between their XRD patterns. The intensities of the peaks of Cr/γ-Al_2O_3 and Mn/γ-Al_2O_3 were high, but a slight decrease in the intensity of sharp peaks was observed. No crystalline manganese oxide or chromium oxide phases were observed for Mn/γ-Al_2O_3 and Cr/γ-Al_2O_3, the broad diffraction peaks being attributed to γ-Al_2O_3.[20,21] These results indicate the good dispersion of metal species (manganese and chromium) on alumina.

In addition, using the Scherrer formula, the mean particle size of γ-Al_2O_3 was calculated to be 30 nm through 2θ of $67.16°$. The particles of both catalysts were estimated, therefore, to be in the nanometer range (≤ 100 nm).
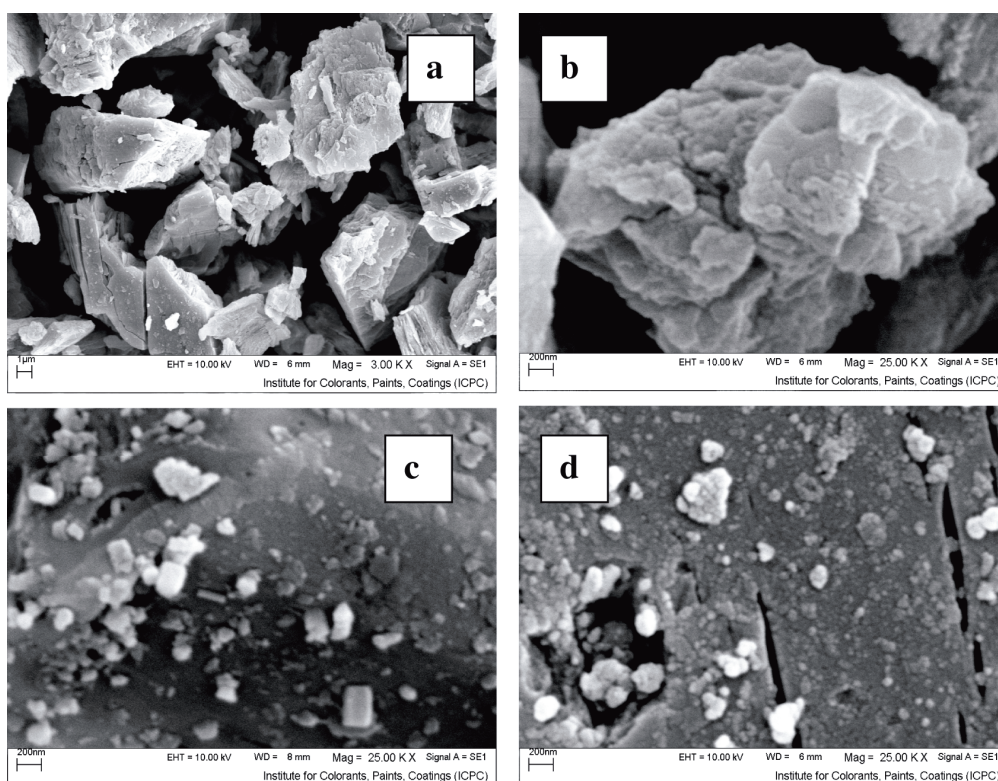
Figure 1. SEM images of catalysts: a) γ-Al$_2$O$_3$ (1 μm), b) γ-Al$_2$O$_3$ (200 nm), c) Cr/γ-Al$_2$O$_3$ (200 nm), and d) Mn/γ-Al$_2$O$_3$ (200 nm).
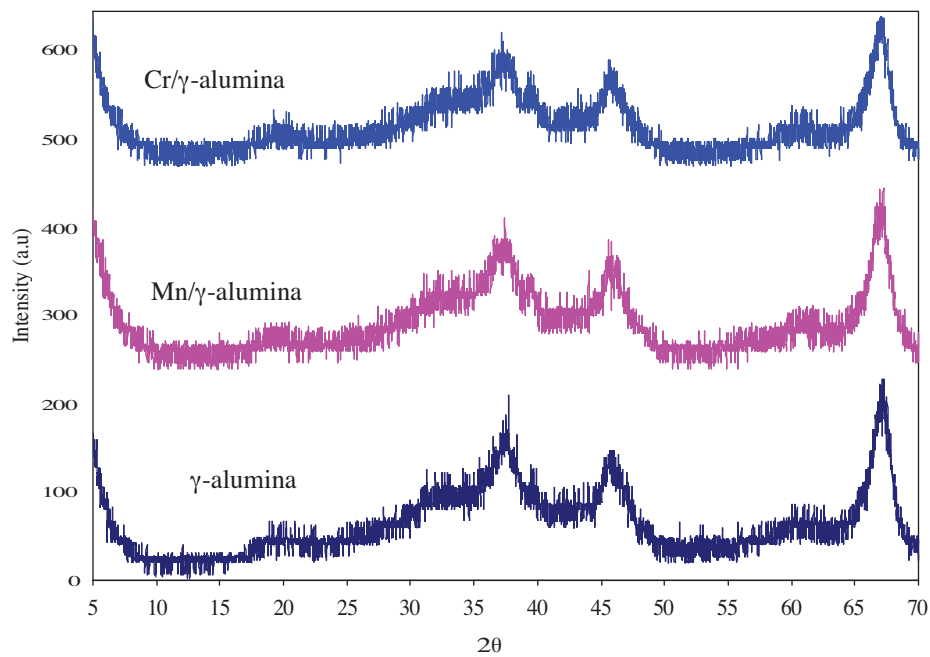

Figure 2. XRD pattern of catalysts.

Furthermore, through the XRD patterns of the catalysts, relative crystallinity was calculated on the basis of comparing the average intensities of the most intense peaks for pure γ-Al$_2$O$_3$ versus the modified catalysts. The initial pure γ-Al$_2$O$_3$ was assumed to be 100% crystalline. The degree of crystallinity of Mn/γ-Al$_2$O$_3$ and Cr/γ-Al$_2$O$_3$ catalysts was identified utilizing the main X-ray diffraction peak (67.16°) via Eq. (1):

$$\text{Crystallinity (\%)} = \frac{\text{peak intensity of product}}{\text{peak intensity of reference sample}} \times 100. \tag{1}$$

Table 2 shows the results of XRD analysis. In this table, "I" denotes the intensity and "d" is the spacing between the planes in the atomic lattice. The ratios of I$_{Cr/\gamma-Al2O3}$ to I$_{\gamma-Al2O3}$ and I$_{Mn/\gamma-Al2O3}$ to I$_{\gamma-Al2O3}$ decreased when Cr and Mn oxides were introduced. The relative crystallinity of the catalysts decreased because of the amorphous phase of the chromium and manganese oxides. Furthermore, a slight decrease in the d-value was observed, such that d$_{Cr/\gamma-Al2O3}$/d$_{\gamma-Al2O3}$ and d$_{Mn/\gamma-Al2O3}$/d$_{\gamma-Al2O3}$ became 0.98 and 0.99, respectively.

Table 2. XRD properties of catalysts.

Catalyst	d$_{M/\gamma-Al2O3}$/d$_{\gamma-Al2O3}$	I$_{M/\gamma-Al2O3}$/I$_{\gamma-Al2O3}$	Relative crystallinity
Cr/γ-Al$_2$O$_3$	0.98	0.85	85
Mn/γ-Al$_2$O$_3$	0.99	0.9	90

Catalytic studies of O-VOCs in single form

In complete catalytic oxidation, VOCs react with oxygen in the presence of a catalyst, leading to H$_2$O and CO$_2$ without the formation of any by-product. In such a process, partial oxidation should be avoided. But at lower temperatures, a little by-product is observed. The main by-products of isopropanol and ethyl acetate oxidation are propene and acetaldehyde, respectively. Benzyl alcohol gives rise to carbon monoxide and carbon dioxide as the only carbon-containing products.

Figures 3-5 present the conversion of O-VOCs on γ-Al$_2$O$_3$, Cr/γ-Al$_2$O$_3$, and Mn/γ-Al$_2$O$_3$, respectively. These show that the conversion of organic compounds on Cr- and Mn-supported catalysts was higher than the conversion on γ-Al$_2$O$_3$, indicating an improvement in catalytic activity with the introduction of Cr and Mn. The following order resulted for the activity of catalysts: γ-Al$_2$O$_3$ < Cr/γ-Al$_2$O$_3$ < Mn/γ-Al$_2$O$_3$. The higher activity of Mn/γ-Al$_2$O$_3$ is attributed to the capability of manganese to form oxides with different oxidation states and high oxygen storage capacity. The higher activity is primarily due to high efficiency in the reduction/oxidation cycles.[22] Furthermore, the results showed that for the Mn/γ-Al$_2$O$_3$, the complete conversion of O-VOCs to carbon dioxide and water occurred in comparison with other catalysts, especially at higher temperatures.

In all catalytic studies, isopropanol showed the highest reactivity, and the conversion of the ethyl acetate was the lowest. The order of activity of organic compounds for conversion on a catalyst was as follows: ethyl acetate < MEK < benzyl alcohol < isopropanol.
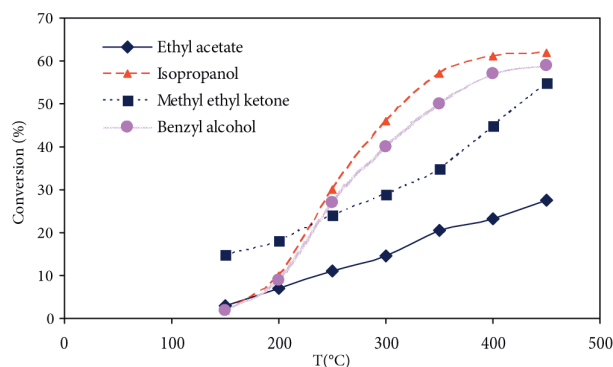
Figure 3. Conversion of organic compounds over γ-Al_2O_3.
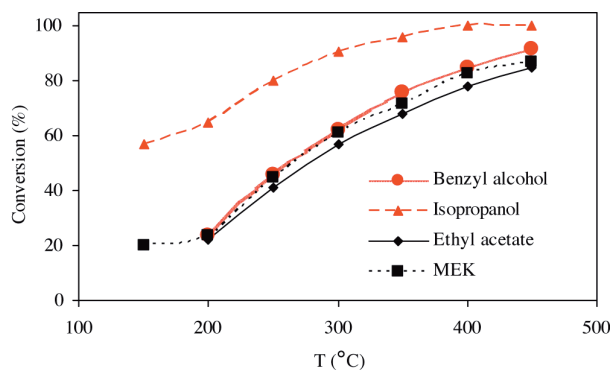
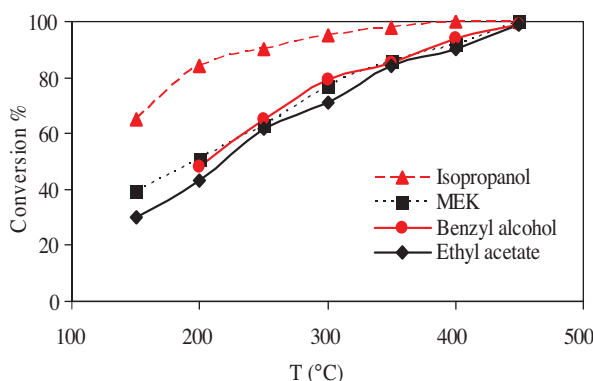**Figure 4.** Conversion of organic compounds over Cr/γ-Al_2O_3.

Figure 5. Conversion of organic compounds over Mn/γ-Al_2O_3.

The higher reactivity of isopropanol and benzyl alcohol was attributed to the relatively higher activity of the hydroxyl group compared to the carbonyl group in MEK and ethyl acetate (reactivity: $SP^3 > SP^2$). Thus, isopropanol and benzyl alcohol could easily interact with the vacant p-orbitals of chromium and manganese, leading to the breakage of the C-O bond in the molecule.[23] The relatively lower activity of benzyl alcohol compared to isopropanol can be attributed to the occurrence of the resonance effect in its ring, leading to the relative stability of molecules.

The difference in catalytic activities of organic compounds is due to the different structure and nature of organic compounds. When isopropanol is adsorbed on the metal oxides supported on catalysts (acting as Lewis acid sites), the probability of adsorption of the OH group of the molecule on the metal oxide will be more than that of the hydrogen of the molecule. Isopropanol, which possesses an OH group, will certainly be more strongly adsorbed on the catalysts.

Catalytic studies of O-VOCs in binary mixtures

Volatile organic compounds are emitted from many different sources, and their formation processes are not always catalyzed. These compounds are usually found as mixtures of compounds in the atmosphere. Since the oxidation behavior of these compounds in the single form differs from that in mixtures, we investigated the

oxidation behavior in mixed forms.[3,19] In order to determine the inhibition/promotion effect of each organic compound on the other's oxidation over a catalyst, it is common to consider the VOC binary mixture.[3,19] Therefore, we considered VOC binary mixtures of isopropanol/benzyl alcohol (the most reactive and mean reactive components, respectively) and MEK/benzyl alcohol (the least reactive and mean reactive components) with different natures on the most active catalyst (Mn/γ-Al_2O_3). Figure 6 shows the light-off curves for isopropanol/benzyl alcohol (solid line) and MEK/benzyl alcohol (dashed line) oxidations. It was observed that the conversion of isopropanol was significantly improved while that of benzyl alcohol dropped, when presented together. In the case of MEK/benzyl alcohol oxidation, the conversion of MEK increased as compared to conversion in single form, where the conversion of benzyl alcohol decreased. An inhibition and promotion effect was observed for the oxidation of O-VOC binary mixtures compared to that of single forms. Some researchers have pointed out competitive adsorption as the main reason for the inhibition/promotion effect in binary VOC mixtures.[23] When present together, isopropanol/benzyl alcohol and MEK/benzyl alcohol molecules competed with each other for chemisorption on active sites in favor of the former, due to its nucleophilicity. In addition, for medium-pore alumina, the effect of shape selectivity could not be totally ruled out as the shape of the relatively linear isopropanol and MEK molecules enabled them to diffuse much more easily.[23]

The effect of water vapor as a co-feed on the catalytic conversion of isopropyl alcohol, as the most reactive compound, was studied, and the result is shown in Figure 7. It was observed that the presence of water vapor as a co-feed negatively affected the conversion of isopropyl alcohol. The inhibitive effect of water on VOC conversion was attributed to competitive adsorption between these 2 types of substances. In addition, the effect of water vapor was also temperature-dependent, as a reduction in conversion occurred with an increase in reaction temperature.
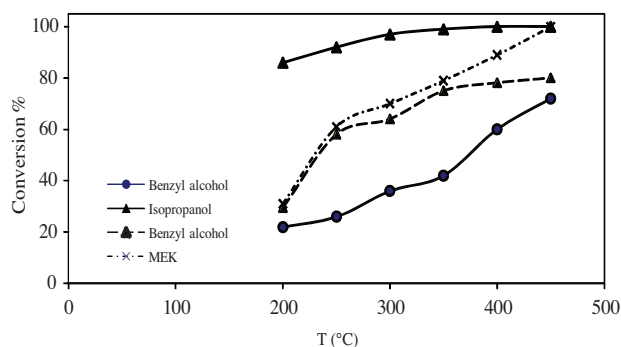

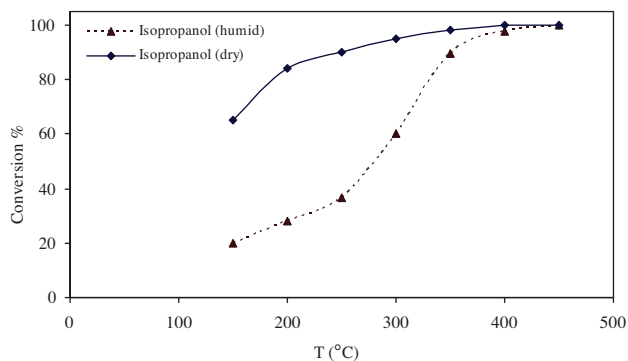**Figure 6.** Conversion of binary mixture of isopropanol/benzyl alcohol and MEK/benzyl alcohol on Mn/γ-Al_2O_3.

Figure 7. Light-off curves for isopropanol conversion under dry and humid feed stream on Mn/γ-Al_2O_3.

The interaction of sorbate molecules (isopropyl alcohol and water) with sorbent (Mn/γ-Al_2O_3) can occur in the form of van der Waals forces and electrostatic forces. Water molecules also have a cluster-forming ability around active sites, thereby creating a diffusion block for VOC molecules. At higher temperatures, this localization might be prevented, and consequently the deactivation effect by water molecules might be diminished.[21]

Conclusion

This study revealed the catalytic role of transition metals supported on γ-Al_2O_3, and the higher performance of Mn/γ-Al_2O_3 was concluded. This study was in agreement with our previous studies,[2,3] which confirmed that nanocatalysts present much higher activity than other catalysts. It was concluded that the shape and structure of O-VOCs are important factors leading to reactivity and conversion efficiency. Competitive adsorption is the main reason for the inhibition/promotion effect in binary mixtures. Furthermore, the inhibition influence of water vapor on O-VOCs conversion was temperature-dependent, decreasing at increased temperatures.

It was concluded that catalytic activity is not related to the BET surface area of the catalyst, while it does depend on the type of metal and its loading content.

Acknowledgment

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