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EXCLUSIVE EFFECT OF DIFFERENT TRANSITION METALS SUPPORTED ON WTi-PILLARED CLAY: SURFACE ACIDITY AND REDOX PROPERTIES

Souissi, M. and *Khalfallah Boudali, L.

University of Tunis El Manar, Faculty of Sciences of Tunis, Department of Chemistry, Laboratory of Materials Chemistry and Catalysis. Campus Farhat Hached of Tunis, 1060 Tunis, Tunisia

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ABSTRACT

Different transition metals (Mo, Cu, Mn,Ce, V, Co,Zr) supported on WTi-pillared clay were characterized by different techniques and tested in the selective catalytic reduction of nitrogen oxide by ammonia. The effects of diverse transition metals on the textural parameters, the acidity and the redox propertieswerecompared to, then correlated with the catalytic activities. The results demonstrate that the surface propertiesof the investigated materials are largely dependenton the type of transition metal added to the support. The vanadium addition significantly improves the total acidity, which were beneficial for the selective catalytic reduction of nitrogen oxide by ammonia. However, the presence of copper enhances largely the catalyst redox capacity compared to all the other transition metals. The reactivity of the samples containing the metal follows this order: V >> Cu > Ce > Mo > Mn > Co ≈ Zr ≈ the support. The highest efficiency of the best catalysts is directly related to the strongest acidity with moderate redox properties or the inverse.

INTRODUCTION

In recent years, porous materials prepared from the pillared clays have found a wide range of potential application sespecially in heterogeneous catalysis (Gil *et al.*, 2000). The modification of the interlayer space of the starting clay by insertion of the polyoxocations species between the layers followed by calcination at high temperature gives rise to porous materials with attractive properties. The texture, the surface acidity and the thermal stability of the initial clay can be widely improved by the pillaring process. Much research has been carried out on pillared clays with one or two chemical elements. Currently, the number of potential applications of pillared clayswith mixed transition metalsis continuously increasing. Recently, mixed pillared clays such as S/FeCr-PILC (Mishra *et al.*, 2006), S/FeMn-PILC (Mishra *et al.*, 2008), AlCu-PILC and AlFe-PILC (Galeano *et al.*, 2010), ZnTi-PILC (Wang *et al.*, 2011), CrTi-PILC (Zhang *et al.*, 2013), ZrTi-PILC (Bahranowski *et al.* 2015), FeTi-PILC (Li *et al.* 2015), VAl-PILC (Balci *et al.*, 2015), CrCe-Ti-PILC

Corresponding author: **Khalfallah Boudali, L.**
University of Tunis El Manar, Faculty of Sciences of Tunis, Department of Chemistry, Laboratory of Materials Chemistry and Catalysis. Campus Farhat Hached of Tunis, 1060 Tunis, Tunisia

(Zuo *et al.*, 2015), (Pd,Cr)/ [ZrTi]-PILC (Michalik-Zym *et al.*, 2015), (Ce-Mn)/Ti-PILC(He *et al.*, 2016) and (La,Se,Rb)/Ti-PILC (Barama *et al.*, 2017) have been evaluated in different processes. Among the most studied applicationsin research laboratories, we find the selective catalytic reduction of nitrogen oxide (SCR-NO) by ammonia. NO is a toxic gas and a dangerous pollutant. The interest in the SCR-NO reaction is reflected in the number of published papers each year. It is well known that the reduction of NO by ammonia is catalyzed by acid and/or redox sites. The commercial catalysts of this reaction are V_2O_5-WO_3-TiO_2 or V_2O_5-MoO_3-TiO_2 in which TiO_2 supports the oxides V_2O_5 and WO_3 or MoO_3 (Pârvulescu *et al.*, 1998; Busca *et al.*, 1998). However, TiO_2 has a small surface area, low porosity and little resistance to sintering with only Lewis acidity compared to Titanium pillared clay (Ti-PILC) which offers a better surface area, porosity, thermal stability and two kinds of acidity (Lewis and Bronsted). In this context, considerable efforts have been made to replace TiO_2 by Ti-PILC to get an efficient catalyst support (Grzybek, 2007). More recently, Ferjani and Khalfallah Boudali (2016) have investigated the effect of different tungsten amount on the surface properties of WTi-pillared clay. The tungsten is added to increase the thermal stability and acidity of the WTi-

pillared clay. To the present time, there has not been any published work describing the preparation and characterization of diverse transition metals supported on WTi-pillared clay, nor discussing their catalytic activity in any chemical reaction. In this work, the surface acidity and redox properties of various transition metals: Mo, Ce, Mn, Cu, V, Co, Zr supported on WTi-PILC are investigated then correlated with the reactivity of these solids in the selective catalytic reduction of nitrogen oxide by ammonia.

MATERIALS AND METHODS

Materials

The starting material is a commercial Bentonite, provided by Sigma Aldrich.The tungsten solution (10^{-2}M) was prepared by dissolving ammonium metatungstate $(NH_4)_6H_2W_{12}O_{40}$ in distilled water. The Ti-solution was obtained by slowly adding $TiCl_4$ into HCl solution (6M) under vigorous stirring. Final concentrations in titanium (0.82M) and in acid (0.2M) were reached by adding water. To prepare the mixed intercalated claywith tungsten and titanium, the W-solution and the Ti-solutionwere simultaneously added drop wise to the suspension of 2 g clay/500 cm^3 water under vigorous stirring at room temperature. The desired percentage of tungsten added to the clay is 10%and the Ti/clay ratio equals10 mmol/g clay. After 24 h stirring, the solid fraction was separated by centrifugation and filtration, and then it was washed several times with distilled water and dried at room temperature. In the next step the transition metal in aqueous solution (2%) was introduced into the intercalated clay, by incipient wetness impregnation method, under stirring at room temperature.The transition metal (Mo, Cu, Mn, Ce, V, Co, Zr) sources areammonium heptamolybdatetetrahydrate, copper (II) chloride, manganese (II) chloride, cerium (III) chloride, ammonia vanadate, cobalt (II) chloride and zirconium (IV) chloride, respectively. Finally, all the samples are calcined at 500°C at a heating rate of 2°C min^{-1} for 3h under air flow. The samples are referenced as TM/WTi-PILC in which TM = Mo, Cu, Mn, Ce, V, Co, Zr and WTi-PILC is the support.

Characterization and activity

The texture of the samples was determined by nitrogen physisorption using a Micromeritics ASAP 2020 instrument. The samples were outgassed in vacuum during 5 h at 200°C prior to nitrogen physisorption. The total acidity was evaluated by ammonia temperature programmed desorption (NH$_3$-TPD) using an AUTOCHEM 2910 (Micromeritics). Before NH$_3$ adsorption, the samples were pre-treated under air flow (30mL min^{-1}) at 450°C (10 °C min^{-1}) for 30 min. Ammonia adsorption was carried out at 100°C by exposure to 5 vol% NH$_3$ in He (30 mL min^{-1}) for 45 min and then flushed with He for 2 h to remove the remaining adsorbate in the gas phase and physisorbed on the catalyst surface. Finally, ammonia was desorbed in helium flow (30 mL/min) from 100 to 450°C using a heating rate of 10 °C min^{-1}. The temperature programmed reduction by hydrogen (H$_2$-TPR) is frequently used to study the redox properties of the catalysts. This technique has been carried out in the AUTOCHEM 2910. The sample was outgassed in an argon flow at 500 °C, and kept constant at this temperature for 40 min. Then, it was cooled to room temperature and stabilized under an argon/hydrogen flow. The temperature and thermal conductivity detector signals were then continuously recorded during heating at 15

°C min^{-1} to 700 °C. The products formed during the reduction process were retained by a cooling trap placed between the sample and the detector. The catalytic tests were performed in a continuous flow fixed-bed microreactor operating at atmospheric pressure. The sample (0,050 g) was activated in situ at 500 °C under He then cooled to room temperature. A feed gas stream containing NO (1000 ppm), NH$_3$ (1000 ppm), O$_2$ (8%) and H$_2$O (3,5%)in He as balance gas was supplied to the microreactor through mass flow controllers. The total flow rate was 100 mL min^{-1} and the selective catalytic reduction of nitrogen oxide (SCR-NO) was carried out on programmed temperature from room temperatureup to 500°C with a heating rate of 6°C min^{-1}. The reaction products were analyzed by sampling on line with a quadruple mass spectrometer (Pfeiffer Omnistar), calibrated with standard mixtures and by recording the following masses: NO (30), N$_2$ (28), N$_2$O (44), NO$_2$ (46), NH$_3$ (17), O$_2$ (32) and H$_2$O (18).

RESULTS AND DISCUSSION

The textural properties of the samples investigated in this work are presented in Table 1. The BET surface area of the starting clay is very low (25m^2/g) without porosity. The remarkable increase in the surface area and the porosity of the WTi-PILC support indicates a success of the pillaring process. The addition of a transition metal (Mo, Cu, Mn,Ce, V, Co, Zr) induces also an increase in the BET surface area and the total pore volume.

Table 1. Textural properties of the starting clay and the pillared clays calcined at 500°C.

Samples	S_{BET} (m^2 g^{-1})	V_p (cm^3 g^{-1})	D_p (Å)
Starting clay	25 (n.c)	-	-
WTi-PILC	242	0.103	38.855
Ce/WTi-PILC	232	0.216	41.521
V/WTi-PILC	154	0.214	46.132
Mo/WTi-PILC	296	0.274	43.526
Mn/WTi-PILC	273	0.244	41.824
Zr/WTi-PILC	273	0.167	40.431
Cu/WTi-PILC	272	0.212	41.527
Co/WTi-PILC	224	0.235	41.719

S_{BET} : specific surface area, V_p : pore volume, D_p : pore diameter.
n.c. = non calcined

The surface area of the support WTi-PILC (242 m^2/g) decreased slightly after addition of Co (224 m^2/g) or Ce (232 m^2/g) and diminished significantly (154 m^2/g) after adding vanadium. This may be due to the saturation of some pores by the transition metal species which is more pronounced in the case of vanadium. But the opposite is observed for Mo/WTi-PILC (296 m^2/g) showing an increase in the thermal stability at 500°C after addition of molybdenum. The surface areas are almost the same (273 m^2/g) in the case of the samples prepared with Mn or Zr and Cu. The improvement of the surface areas can be explained by the occurring structural changes after the removal of water from the pillars during the thermal treatments. Both interlayer and inter pillar spacing can be modified during the calcinations steps when dehydration or sintering of pillars occurs. For all the samples, the specific surface areas above 150 m^2/g at 500°C indicate a high thermal stability of these pillared clays. In many industrial applications, the texture plays a decisive role for the catalyst activity. The NH$_3$-TPD profiles of all the investigated samples are presented in Figure 1. The only material prepared with vanadium displays the highest total acidity compared to all the pillared clays investigated in this work. The vanadium shows a

significant increase in the uptake of NH_3 bound to weak and strong acid sites. It is well known that the first peak at around 200°C is related to desorption of NH_3 either physisorbed or linked to weak Bronsted acid sites, while the second one, at higher temperature (>350°C), can be attributed to the desorption of NH_3 from stronger Lewis acid sites. The ammonia species bonded to the Bronsted acid sites are more easily desorbed at low temperature than those bonded to the Lewis acid sites desorbed at high temperature. It is reasonable to conclude that the stronger acid sites on V/WTi-PILC mainly originate from the high acidic properties of V_2O_5. The NH_3-TPD profiles of the Figure 2 demonstrate the dissimilarity of the surface acidity depending on the kind of the transition metal. It is clear that molybdenum and copper are also responsible for the increase in both Lewis and Bronsted acidity. By contrast, the surface acidity of the samples prepared with Mn, Co, Zr is only Bronsted acidity and no remarkable modification was observed after Ce addition. It seems that the cerium does not modify the surface acidity of the support WTi-PILC. Combining these results, the addition of vanadium to the support increases significantly the total acidity, mainly the strong Lewis acid sites of V/WTi-PILC compared to other transition metals studied in this work. The H_2-TPR profiles of all the samples are shown in Figure 3. The differences in the H_2-TPR profiles were due to the type and the strength of interactions between the transition metals and the WTi-PILC support. The reduction peak begins above 350°C for all the investigated pillared clays except the sample Cu/WTi-PILC, which occurs at lower temperature. For the latter, the threshold of hydrogen consumption begins at about 220°C and two peaks were perceived. The first peak, centred at around 260°C, less distinct, is mainly due to the reduction process of copper Cu^{2+} to Cu^+, whereas the second peak, more intense and centred at 400°C, is assigned to the reduction of Cu^+ to copper metallic (Dorado *et al.*, 2006). In this case, the H_2 consumption is larger compared to all the samples. Cu/WTi-PILC possesses a larger amount of reducible sites. The second transition metal responsible for a high surface area of the reduction peak corresponds to the sample prepared with vanadium. The significant peak centred at about 520°C is due to the reduction of different vanadium species. Referring to the bibliography relating to VTi systems, the maximum temperature of reduction peak in the TPR profiles T_{max}<or = 497°C indicates the presence of monomeric V-species. However, the reduction of polymeric V-species takes place at about 40°C, slightly higher than that observed in the case of the monomeric species (Popova *et al.*, 2008).
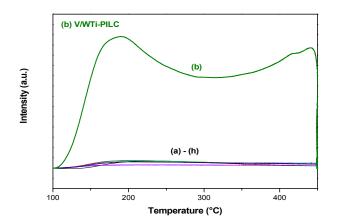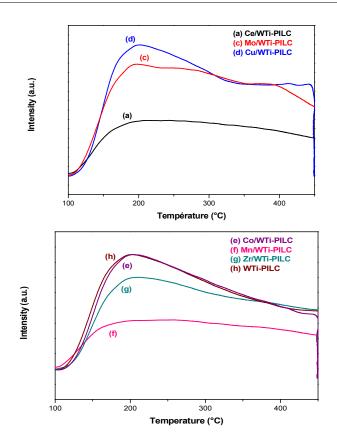

Fig. 2. Comparative study of NH_3-TPD profiles of TM/WTi-PILCs and the support
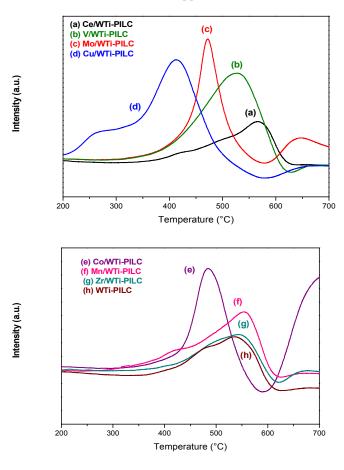

Fig. 3. H_2-TPR profiles of the samples TM/WTi-PILCs

In the case of Ce/WTi-PILC, two TPR peaks around 440 and 560°C appeared. According to the literature (Chen at al., 2009, 2012 ; Liu *et al.*, 2014), these peaks are attributed to the

Fig. 1. NH_3-TPD profilsof: (a - h) TM/WTi-PILCs (TM = Ce, Mo, Cu, Co, Mn, Zr and the support) with (b) V/WTi-PILC

reduction of surface Ce^{4+} to Ce^{3+}. When molybdenum was introduced into the support (Mo/WTi-PILC), the H_2-TPR profile showed two main reduction peaks with maxima near 470°C and 650°C, assigned to the reduction of molybdenum species. The lowest-temperature peak has been attributed to the reduction of Mo^{6+} to Mo^{4+} and the highest temperature peak has been associated with further reduction of Mo^{4+} to Mo^0 (Salerno *et al.*, 2003). With the addition of Mn, two reduction peaks were observed at approximately 420°C and 550°C. The first very weak peak may be associated to the reduction of surface MnO_2 and Mn_2O_3 to Mn_3O_4 while the second one at 550°C may be associated with the reduction of Mn_3O_4 to MnO. This result is consistent with those demonstrated in the literature (Li *et al.*, 2005 ; Kwon *et al.*, 2015 ; Sun *et al.*, 2018). For the sample Co/WTi-PILC, the two reduction peaks observed at 470°C and 690°C can be attributed to the reduction of Co_3O_4 to CoO and further to metallic Co (Romar *et al.*, 2016).

Higher reduction temperatures can be taken as indicative of great interaction between cobalt species and the support WTi-PILC. No remarkable changes were observed after zirconium addition. The H_2-TPR profile of Zr/WTi-PILC showed two reduction peaks, the main is similar to the support (WTi-PILC) whereas the second at about 650°C can be attributed to the reduction peak of zirconium. For pure ZrO_2, only H_2 consumption peak at temperature higher than 500°C (Li *et al.*, 2005) was observed. The TPR peak centered at about 550°C corresponds to reduction of tungsten species of the support WTi-PILC. The area of the peak corresponding to WOx increased to about 575 and 757-790°C with increasing tungsten content (Kwon *et al.*, 2015). It is well known that the reducibility of titanium begins at a temperature higher than 700°C (Reiche *et al.* 2000). In summary, the modification in the redox properties of the support after addition of different transition metals proves that the sample Cu/WTi-PILC displays the best reducibility. The reaction test at different temperature from 150°C to 500°C is the selective catalytic reduction of nitrogen oxide by ammonia (Figure 4). It is clear that V/WTi-PILC is the most active one in the whole temperature range studied. Indeed, the NO conversion follows the sequence: V >> Cu >TM/WTi-PILC, which is in the same order as the NH_3-TPD results proving that the strong acidity is a key factor to reach a high activity at high temperature.
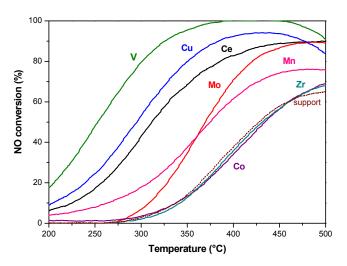

Fig. 4. NO conversion over TM/WTi-PILC (TM = V, Cu, Ce, Mo, Mn, Zr, Co) and the support (WTi-PILC)

The NO conversion of V/WTi-PILC increased with temperature reaction then remained constant at 100% in the wide temperature range of 375-450°C. The reasonable explanation of the best reactivity is related to the highest acidity of V/WTi-PILC, particularly its strong Lewis acid sites and its appropriate redox properties. It is well known, that the reaction mechanism involves a bifunctional pathway composed of NH_3 activation at acid sites and NO activation at redox sites.

The superior acidity of V/WTi-PILC favors the adsorption and activation of the ammonia, therefore enhancing the reduction of NO by NH_3. Several authors attribute to the surface acidity a relevant role in the selective catalytic reduction of NO by NH_3 (Busca *et al.*, 1998; Iwasaki *et al.*, 2018). The sample Cu/WTi-PILC also displays a high catalytic performance. Moreover, the redox property of Cu/WTi-PILC is higher compared to all the samples investigated in this work. Hence, there is a balance between the two kinds of active sites for the SCR-NO reaction: strong acidity and redox ability. For the two best catalysts prepared with V and Cu, the NO conversion declined slightly between 450-500°C due to NH_3 oxidation to NO which generally begins at 300-350°C for the catalysts V/TiO_2 (Busca *et al.*, 1998).

In this work, the ammonia oxidation takes place at about 150°C higher than that observed in the literature. The strong acidity may help to improve ammonia adsorption on catalysts at high temperature and inhibit the NH_3 oxidation to NO. In the case of Ce/WTi-PILC and Mo/WTi-PILC, the NO conversion increases up to 85% at 450°C, then it is maintained constant at 500°C. The catalyst activity at higher temperature is correlated with the surface acidity by contrast at lower temperature the activity is associated with the redox properties. For the sample prepared with Mn, the NO conversion does not exceed 75% between 450-500°C, whereas the addition of Zr or Co seems to have no effect on the catalytic activity of the WTi-PILC support. Among the different catalysts tested, V/WTi-PILC has the most important activity at high temperature. This result confirms that the surface acidity arising from V-species plays a key role in the efficiency of the V/WTi-pillared clay. Moreover, the results confirm that the strong acidity governs the catalyst reactivity in the SCR-NO reaction.

Conclusion

To the best of our knowledge, this is the first work studying different transition metals supported on mixed WTi-pillared clay. The results demonstrate that the surface properties are largely dependent on the kind of transition metal added to the support. After vanadium addition, the total acidity, specifically the strong Lewis acid sites, is remarkably improved compared to all the investigated metals. However, the presence of copper largely enhances the catalyst redox capacity. The results obtained from the reactivity studies follow this order: V >> Cu > Ce > Mo > Mn > Co ≈ Zr ≈ the support (WTi-PILC). The highest efficiency of the best catalysts containing vanadium and copper is directly related to the strongest acidity and the highest redox properties, respectively. In this work, the NH_3 oxidation to NO over V and Cu catalysts takes place at about 150°C higher than that observed in the literature. These results prove that the selective catalytic reduction of NO by ammonia needs a balance of actives sites:stronger acidity with moderate redox properties or the inverse.

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